

PHYS1001B College Physics IB

Thermodynamics IV — The Second Law of Thermodynamics
(Ch. 20)

Introduction



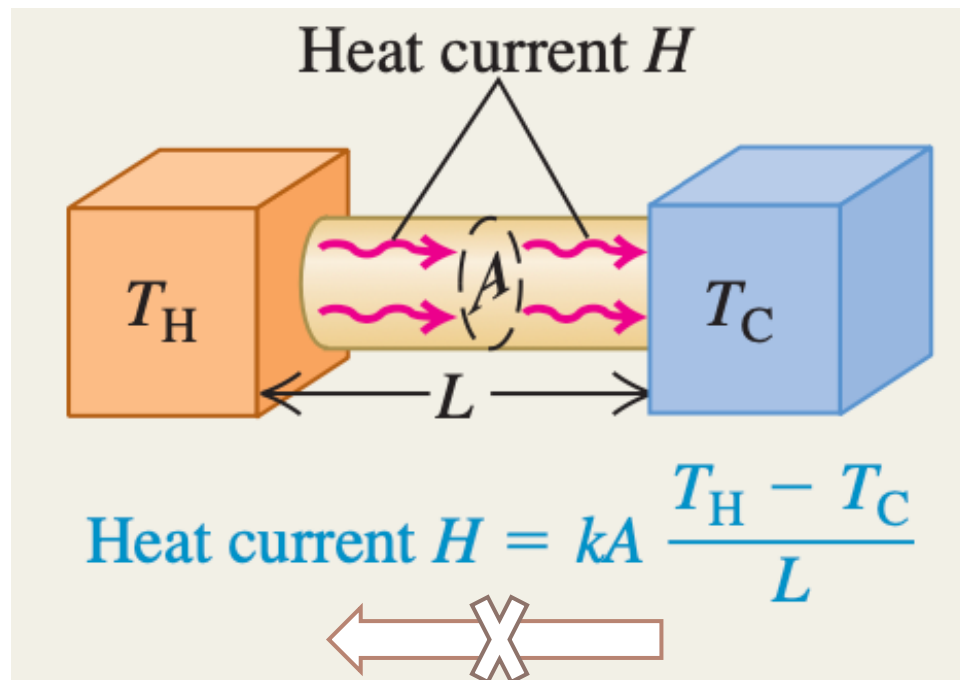
? The second law of thermodynamics tells us that heat naturally flows from a hot body (such as molten lava, shown here flowing into the ocean in Hawaii) to a cold one (such as ocean water, which is heated to make steam). Is it ever possible for heat to flow from a cold body to a hot one?

Outline

- ▶ 20-1 Directions of Thermodynamic Processes
- ▶ 20-2 Heat Engines
- ▶ 20-3 Internal-Combustion Engines
- ▶ 20-4 Refrigerators
- ▶ 20-5 The Second Law of Thermodynamics
- ▶ 20-6 The Carnot Cycle
- ▶ 20-7 Entropy

20-1 Directions of Thermodynamic Processes

Heat flow from a cool body to a hot body would not violate the first law of thermodynamics; energy would be conserved. But it doesn't happen in nature. Why not?

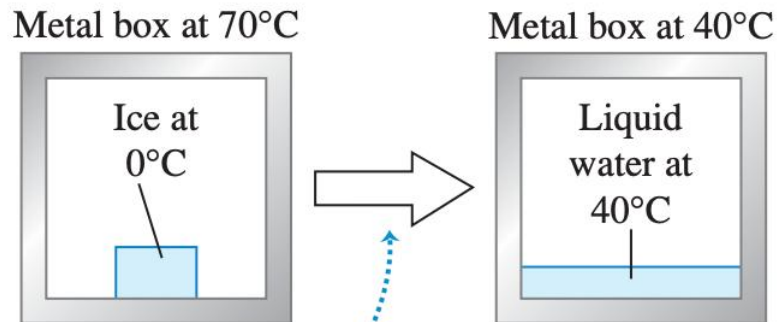


directions of thermodynamic processes: *second law of thermodynamics*

20-2 Heat Engines

Irreversible

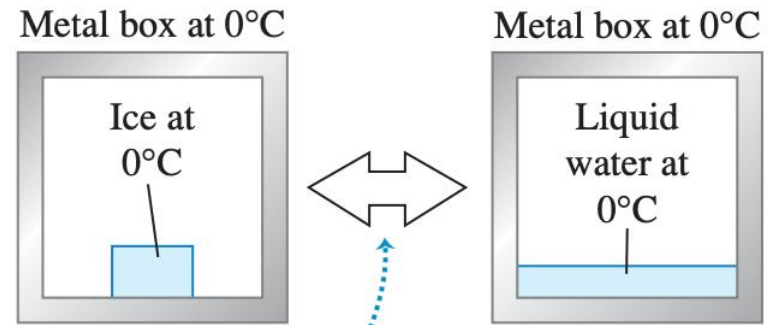
(a) A block of ice melts *irreversibly* when we place it in a hot (70°C) metal box.



Heat flows from the box into the ice and water, never the reverse.

Reversible

(b) A block of ice at 0°C can be melted *reversibly* if we put it in a 0°C metal box.

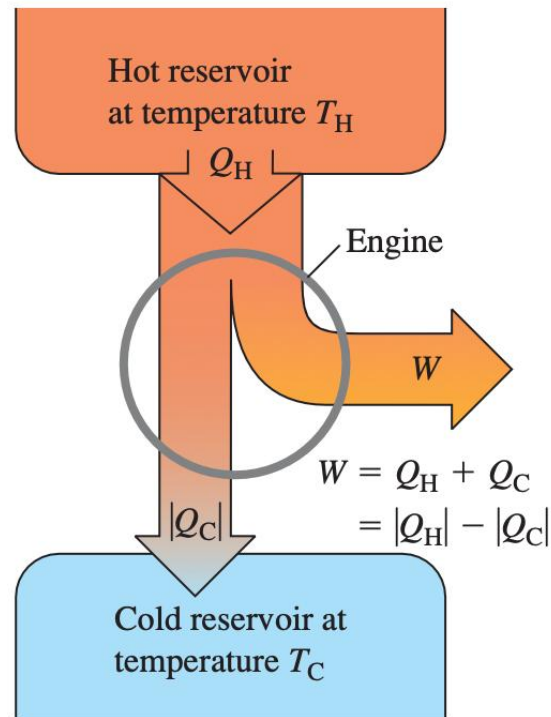


By infinitesimally raising or lowering the temperature of the box, we can make heat flow into the ice to melt it or make heat flow out of the water to refreeze it.

- Thermodynamic processes that occur in nature are all **irreversible processes**.
- Reversible processes are thus **equilibrium processes**, with the system always in thermodynamic equilibrium.

20-2 Heat Engines

20.3 Schematic energy-flow diagram for a heat engine.



$$W = Q = Q_H + Q_C = |Q_H| - |Q_C|$$

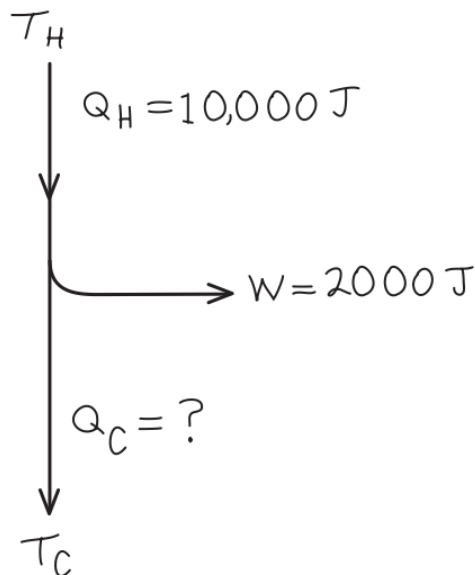
thermal efficiency of an engine

$$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right|$$

Sample Problem

Example 20.1 Analyzing a heat engine

A gasoline truck engine takes in 10,000 J of heat and delivers 2000 J of mechanical work per cycle. The heat is obtained by burning gasoline with heat of combustion $L_c = 5.0 \times 10^4 \text{ J/g}$. (a) What is the thermal efficiency of this engine? (b) How much heat is discarded in each cycle? (c) If the engine goes through 25 cycles per second, what is its power output in watts? In horsepower? (d) How much gasoline is burned in each cycle? (e) How much gasoline is burned per second? Per hour?



EXECUTE: (a) From Eq. (20.4), the thermal efficiency is

$$e = \frac{W}{Q_H} = \frac{2000 \text{ J}}{10,000 \text{ J}} = 0.20 = 20\%$$

(b) From Eq. (20.2), $W = Q_H + Q_C$, so

$$Q_C = W - Q_H = 2000 \text{ J} - 10,000 \text{ J} = -8000 \text{ J}$$

That is, 8000 J of heat leaves the engine during each cycle.

(c) The power P equals the work per cycle multiplied by the number of cycles per second:

$$\begin{aligned} P &= (2000 \text{ J/cycle})(25 \text{ cycles/s}) = 50,000 \text{ W} = 50 \text{ kW} \\ &= (50,000 \text{ W}) \frac{1 \text{ hp}}{746 \text{ W}} = 67 \text{ hp} \end{aligned}$$

(d) Let m be the mass of gasoline burned during each cycle. Then $Q_H = mL_c$ and

$$m = \frac{Q_H}{L_c} = \frac{10,000 \text{ J}}{5.0 \times 10^4 \text{ J/g}} = 0.20 \text{ g}$$

(e) The mass of gasoline burned per second equals the mass per cycle multiplied by the number of cycles per second:

$$(0.20 \text{ g/cycle})(25 \text{ cycles/s}) = 5.0 \text{ g/s}$$

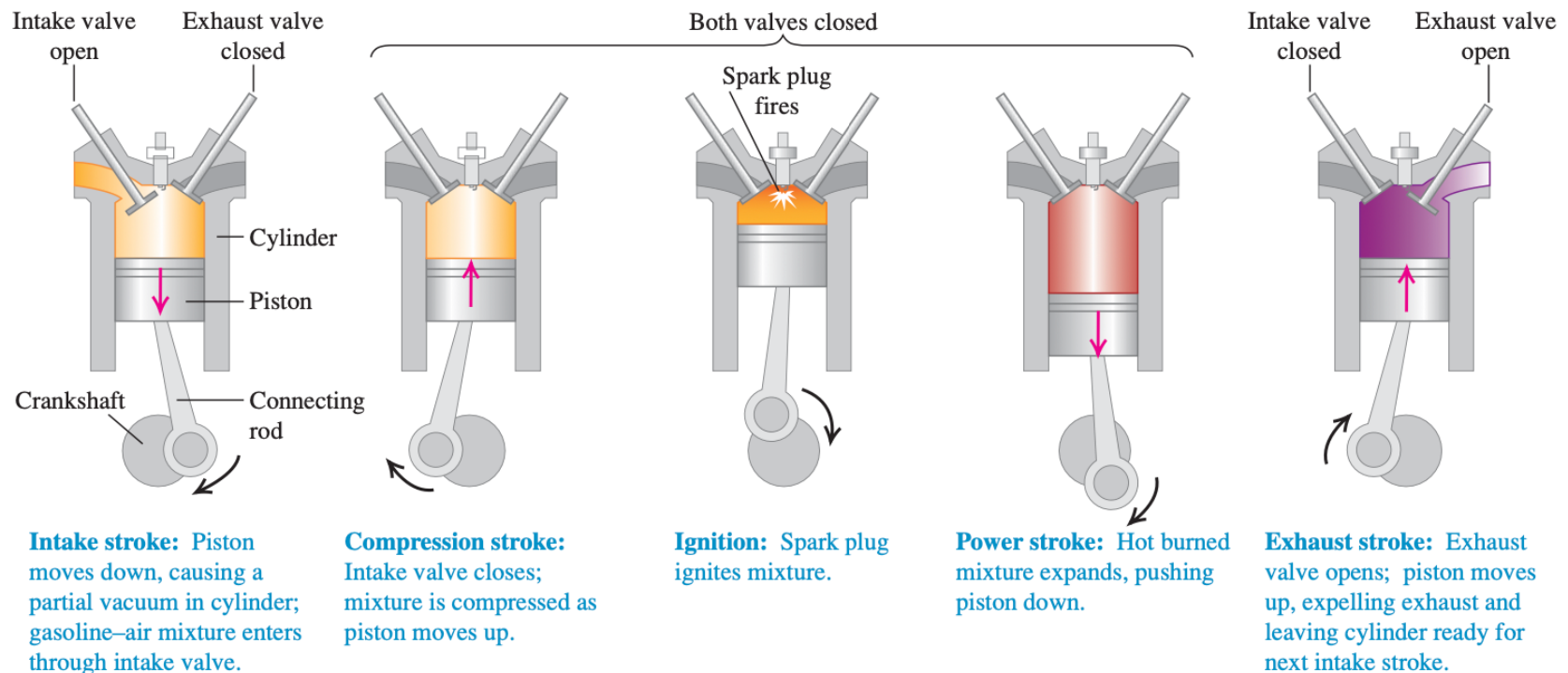
The mass burned per hour is

$$(5.0 \text{ g/s}) \frac{3600 \text{ s}}{1 \text{ h}} = 18,000 \text{ g/h} = 18 \text{ kg/h}$$

20-3 Internal-Combustion Engines

Figure 20.5 shows the operation of one type of gasoline engine. First a mixture of air and gasoline vapor flows into a cylinder through an open intake valve while the piston descends, increasing the volume of the cylinder from a minimum of V (when the piston is all the way up) to a maximum of rV (when it is all the way down). The quantity r is called the **compression ratio**; for present-

20.5 Cycle of a four-stroke internal-combustion engine.



20-3 Internal-Combustion Engines

Otto cycle

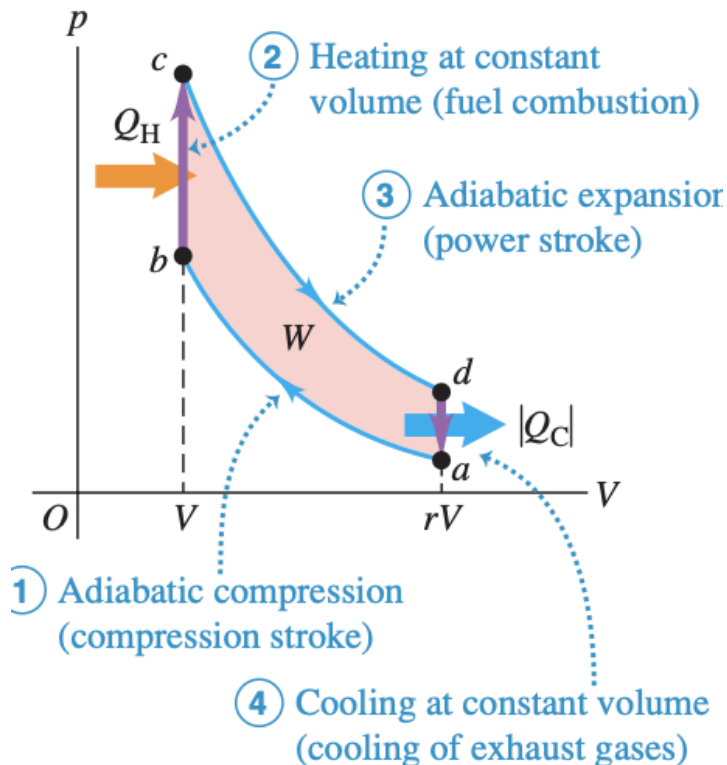
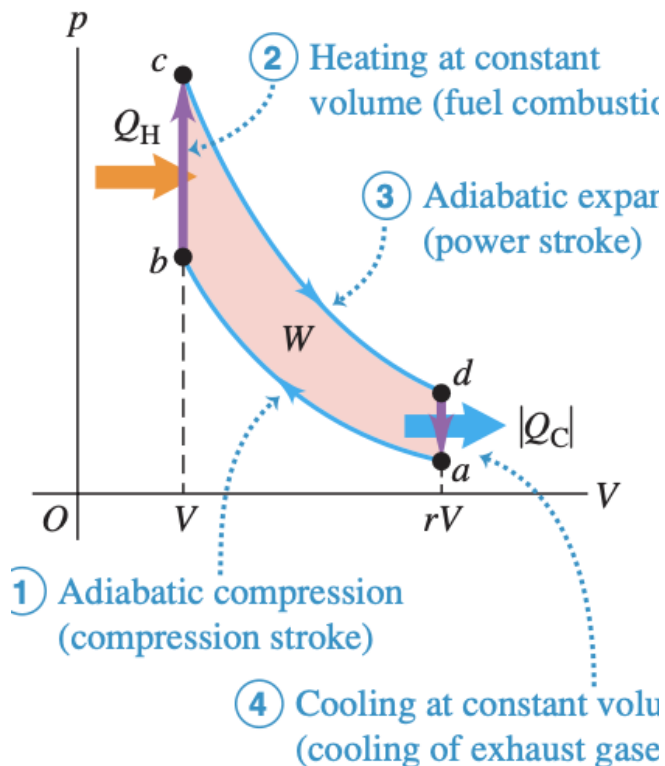


Figure 20.6 is a pV -diagram for an idealized model of the thermodynamic processes in a gasoline engine. This model is called the **Otto cycle**. At point a the gasoline–air mixture has entered the cylinder. The mixture is compressed adiabatically to point b and is then ignited. Heat Q_H is added to the system by the burning gasoline along line bc , and the power stroke is the adiabatic expansion to d . The gas is cooled to the temperature of the outside air along line da ; during this process, heat $|Q_C|$ is rejected. This gas leaves the engine as exhaust and does not enter the engine again. But since an equivalent amount of gasoline and air enters, we may consider the process to be cyclic.

20-3 Internal-Combustion Engines

Otto cycle



We can calculate the efficiency of this idealized cycle. Processes bc and da are constant-volume, so the heats Q_H and Q_C are related simply to the temperatures:

$$Q_H = nC_V(T_c - T_b) > 0$$

$$Q_C = nC_V(T_a - T_d) < 0$$

The thermal efficiency is given by Eq. (20.4). Inserting the above expressions and cancelling out the common factor nC_V , we find

$$e = \frac{Q_H + Q_C}{Q_H} = \frac{T_c - T_b + T_a - T_d}{T_c - T_b} \quad (20.5)$$

To simplify this further, we use the temperature–volume relationship for adiabatic processes for an ideal gas, Eq. (19.22). For the two adiabatic processes ab and cd ,

$$T_a(rV)^{\gamma-1} = T_bV^{\gamma-1} \quad \text{and} \quad T_d(rV)^{\gamma-1} = T_cV^{\gamma-1}$$

We divide each of these equations by the common factor $V^{\gamma-1}$ and substitute the resulting expressions for T_b and T_c back into Eq. (20.5). The result is

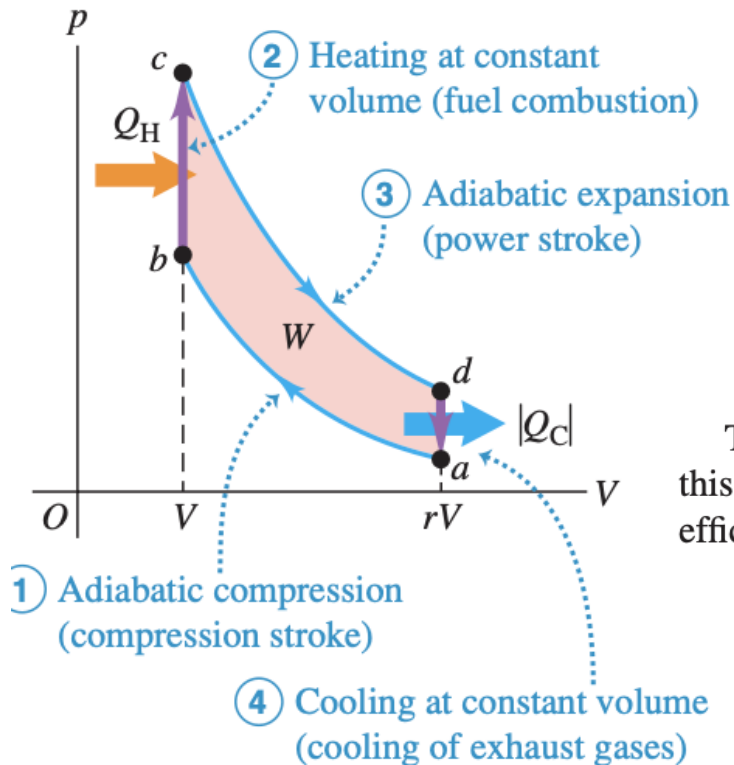
$$e = \frac{T_d r^{\gamma-1} - T_a r^{\gamma-1} + T_a - T_d}{T_d r^{\gamma-1} - T_a r^{\gamma-1}} = \frac{(T_d - T_a)(r^{\gamma-1} - 1)}{(T_d - T_a)r^{\gamma-1}}$$

Dividing out the common factor $(T_d - T_a)$, we get

$$e = 1 - \frac{1}{r^{\gamma-1}} \quad (\text{thermal efficiency in Otto cycle}) \quad (20.6)$$

20-3 Internal-Combustion Engines

Otto cycle

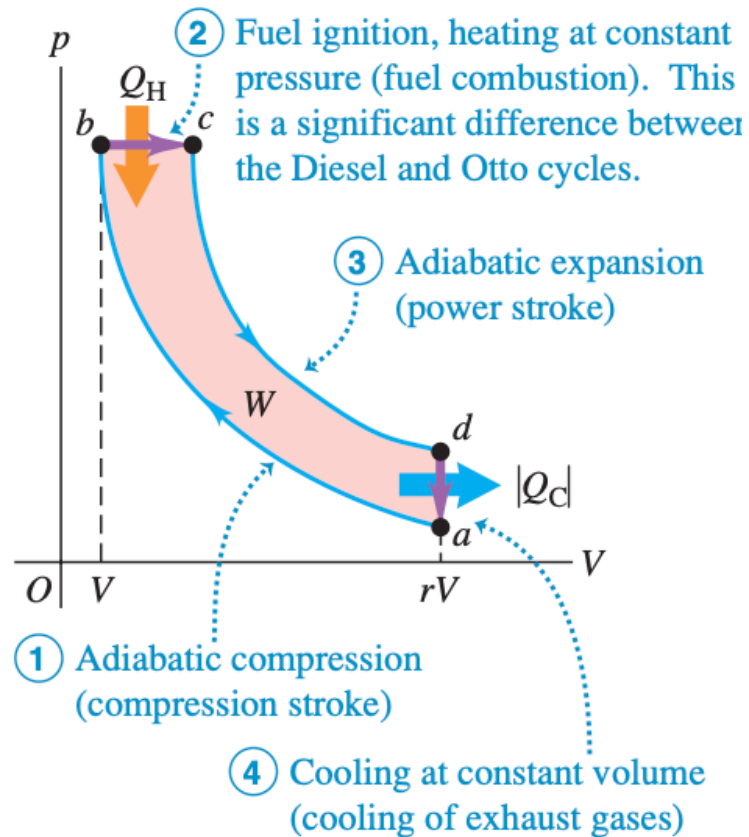


$$e = 1 - \frac{1}{r^{\gamma-1}} \quad (\text{thermal efficiency in Otto cycle})$$

The thermal efficiency given by Eq. (20.6) is always less than unity, even for this idealized model. With $r = 8$ and $\gamma = 1.4$ (the value for air) the theoretical efficiency is $e = 0.56$, or 56%. The efficiency can be increased by increasing r .

20-3 Internal-Combustion Engines

Diesel cycle

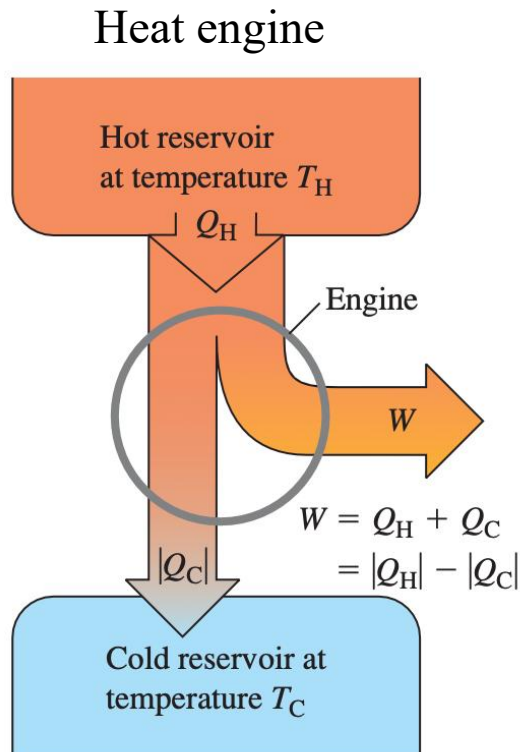


The Diesel engine is similar in operation to the gasoline engine. The most important difference is that there is no fuel in the cylinder at the beginning of the compression stroke. A little before the beginning of the power stroke, the injectors start to inject fuel directly into the cylinder, just fast enough to keep the pressure approximately constant during the first part of the power stroke. Because of the high temperature developed during the adiabatic compression, the fuel ignites spontaneously as it is injected; no spark plugs are needed.

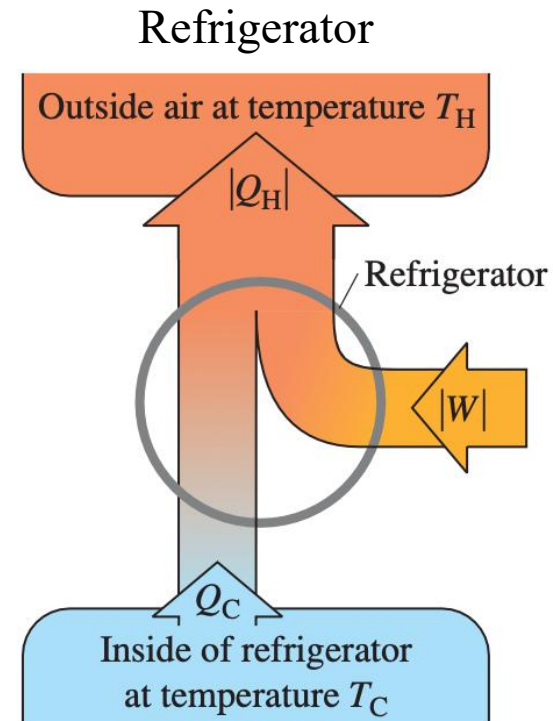
adiabatic compression). Values of r of 15 to 20 are typical; with these values and $\gamma = 1.4$, the theoretical efficiency of the idealized Diesel cycle is about 0.65 to 0.70. As with the Otto cycle, the efficiency of any actual engine is substantially less than this. While Diesel engines are very efficient, they must be built to much tighter tolerances than gasoline engines and the fuel-injection system requires careful maintenance.

20-4 Refrigerators

Comparison

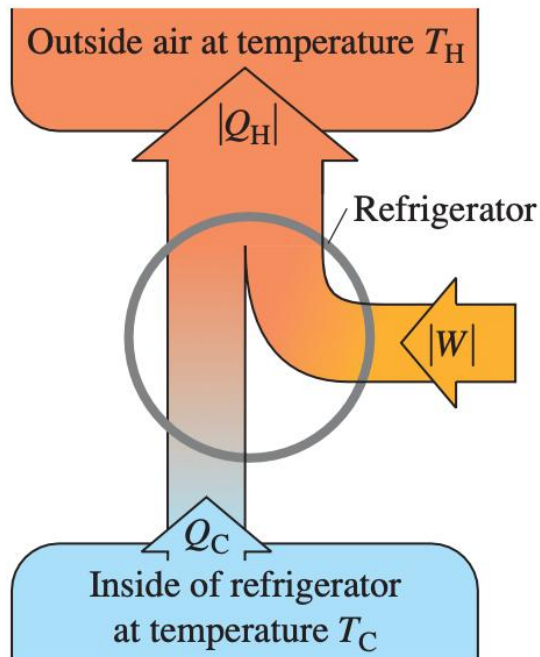


- takes heat from a hot place and gives off heat to a colder place
- a net *output* of mechanical work



- takes heat from a cold place and gives off heat to a warmer place
- a net *input* of mechanical work

20-4 Refrigerators



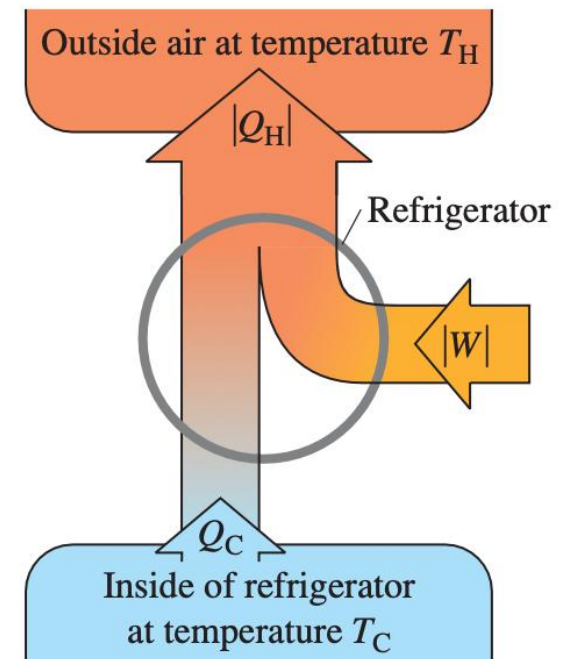
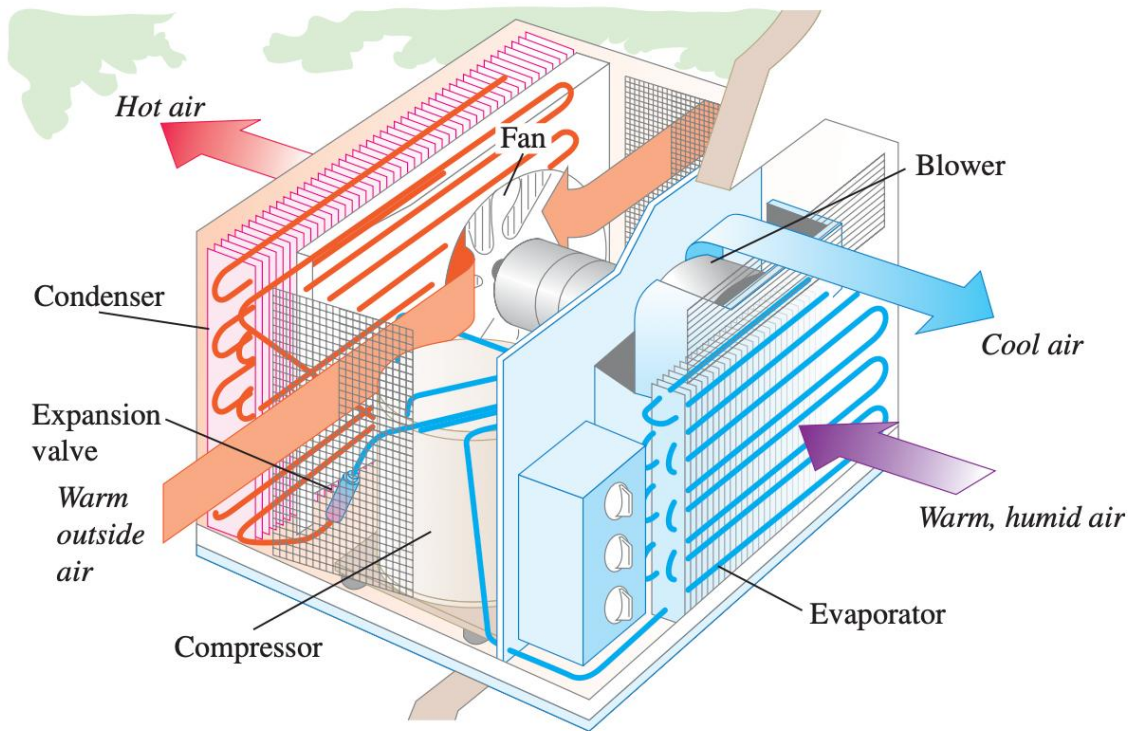
$$|Q_H| = Q_C + |W|$$

Coefficient of performance

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|}$$

- Work is *always* needed to transfer heat from a colder to a hotter body.
- Heat flows spontaneously from hotter to colder, and to reverse this flow requires the addition of work from the outside

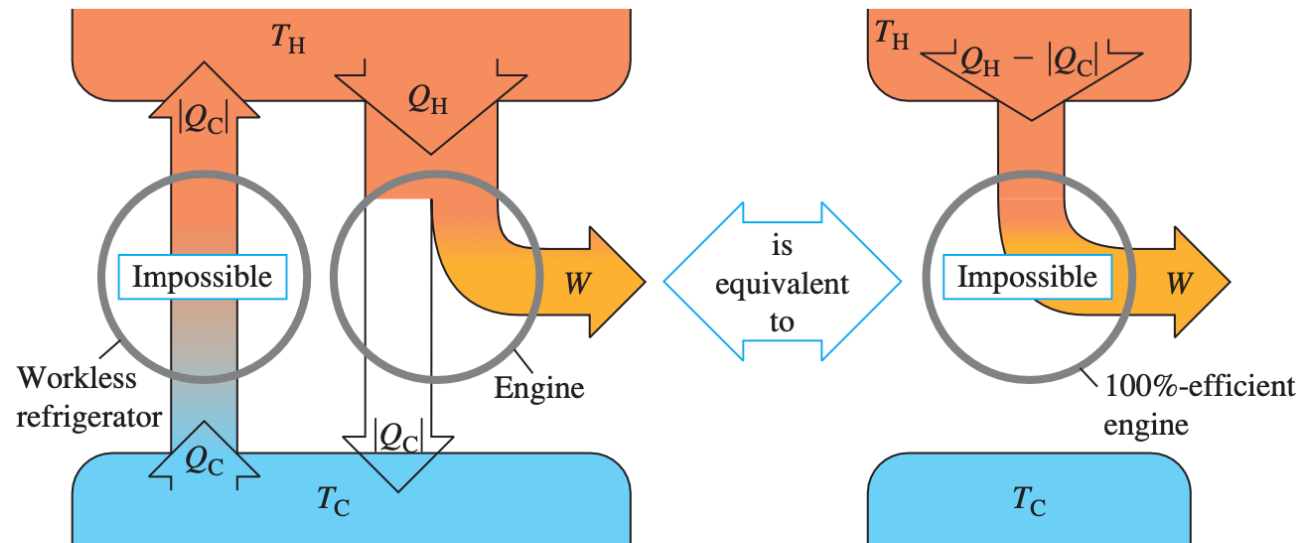
20-4 Refrigerators



20-5 The Second Law of Thermodynamics

“Engine” statement of the second law (*Kelvin–Planck statement*)

It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began.



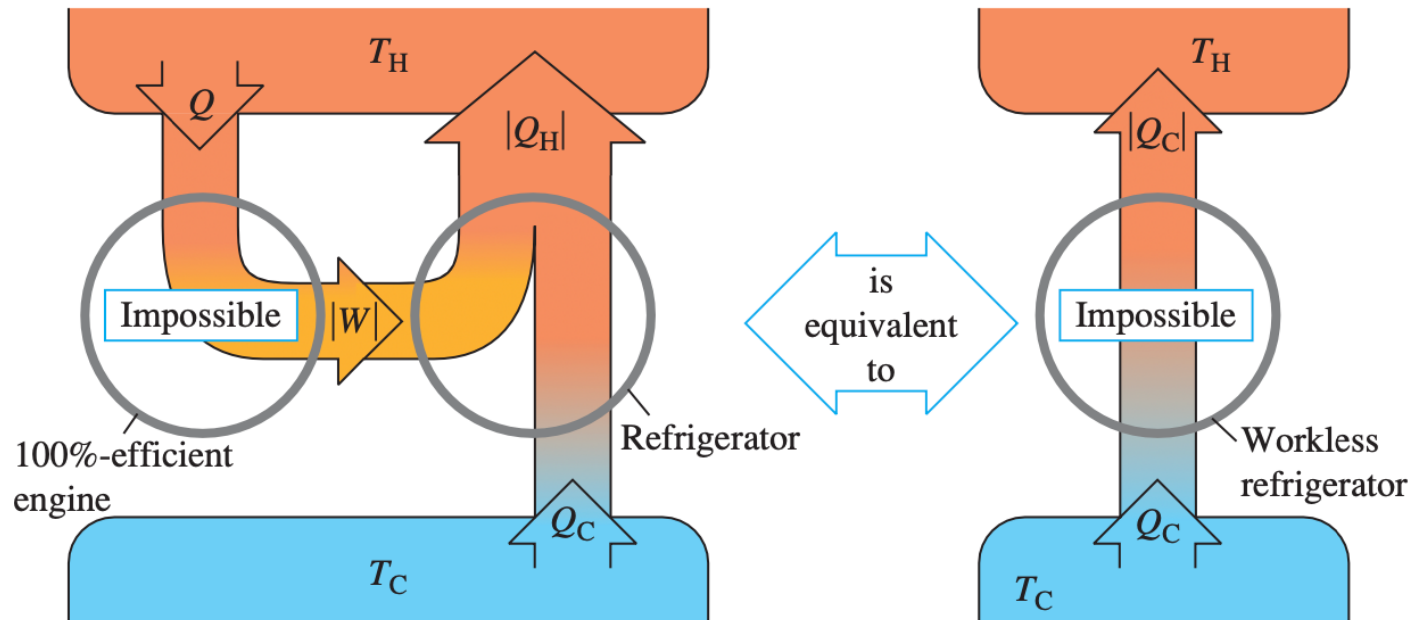
If a workless refrigerator were possible, it could be used in conjunction with an ordinary heat engine to form a 100%-efficient engine, converting heat $Q_H - |Q_C|$ completely to work.

impossible to build a heat engine with 100% thermal efficiency

20-5 The Second Law of Thermodynamics

“Refrigerator” statement of the second law (*Clausius statement*)

It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body.



If a 100%-efficient engine were possible, it could be used in conjunction with an ordinary refrigerator to form a workless refrigerator, transferring heat Q_C from the cold to the hot reservoir with no input of work.

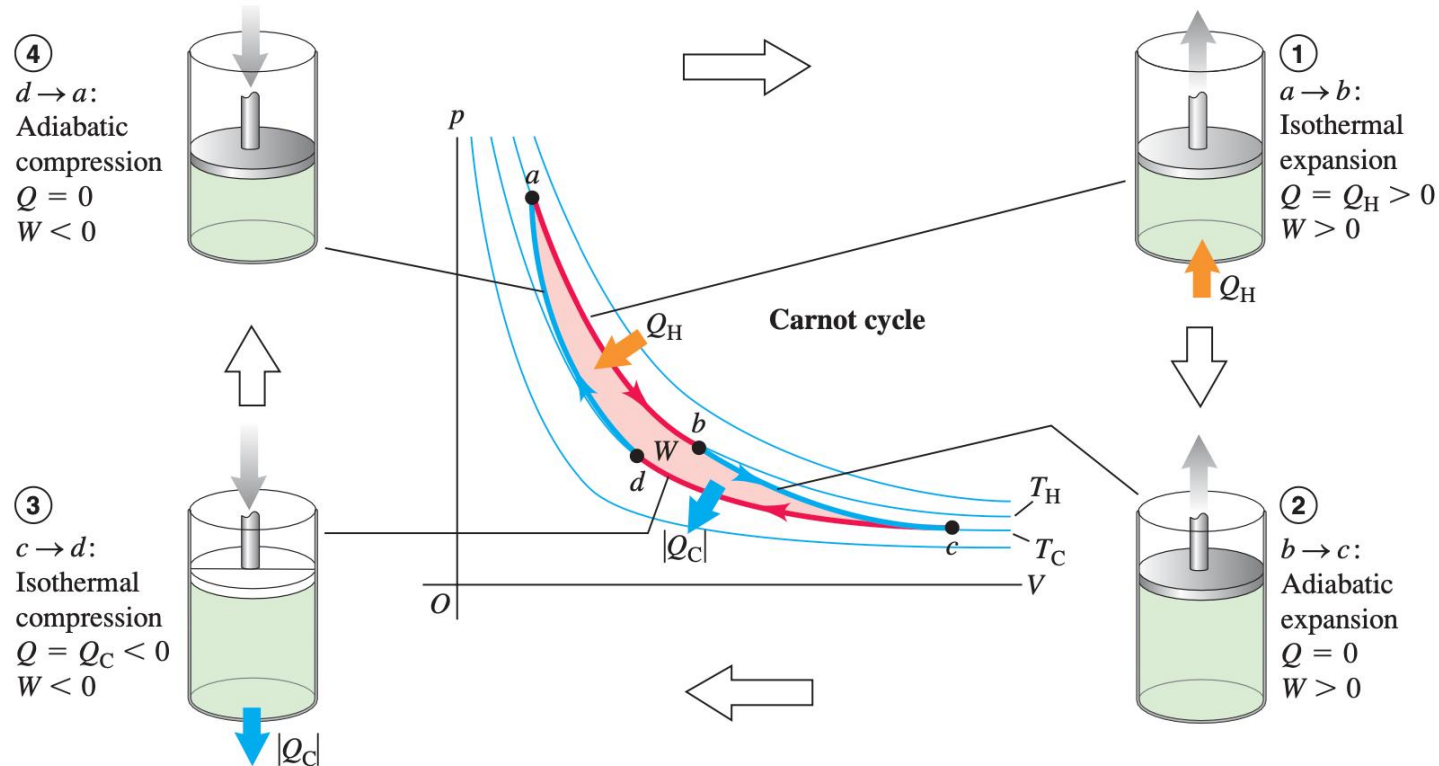
20-6 The Carnot Cycle

Carnot engine: idealized heat engine that has the maximum possible efficiency consistent with the second law

avoid all irreversible processes

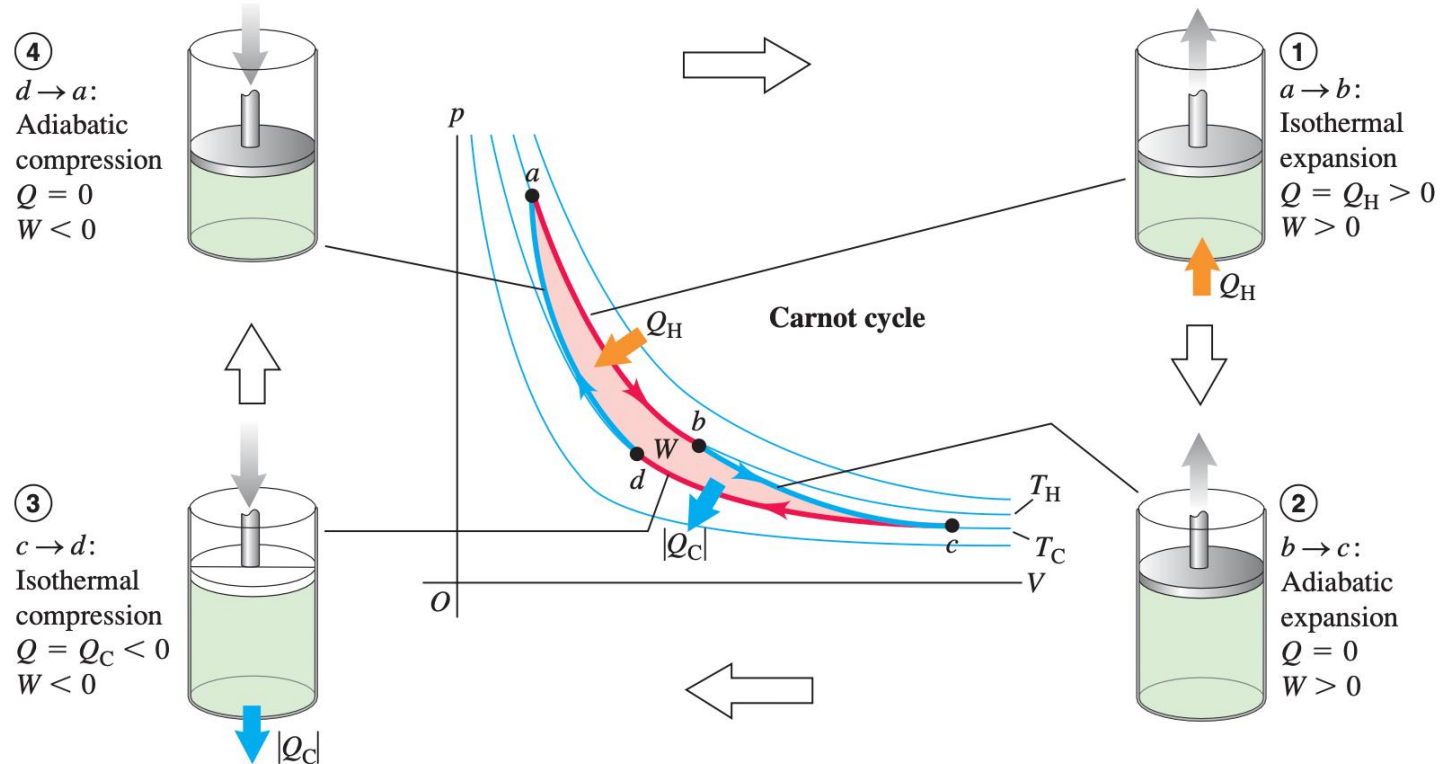
- *Heat flow* through a finite temperature drop is an irreversible process.
- *No* heat transfer between the engine and either reservoir because such heat transfer could not be reversible.
- Carnot Choice: Combination of adiabatic/ isothermal process

20-6 The Carnot Cycle



1. The gas expands isothermally at temperature T_H , absorbing heat Q_H (ab).
2. It expands adiabatically until its temperature drops to T_C (bc).
3. It is compressed isothermally at T_C , rejecting heat $|Q_C|$ (cd).
4. It is compressed adiabatically back to its initial state at temperature T_H (da).

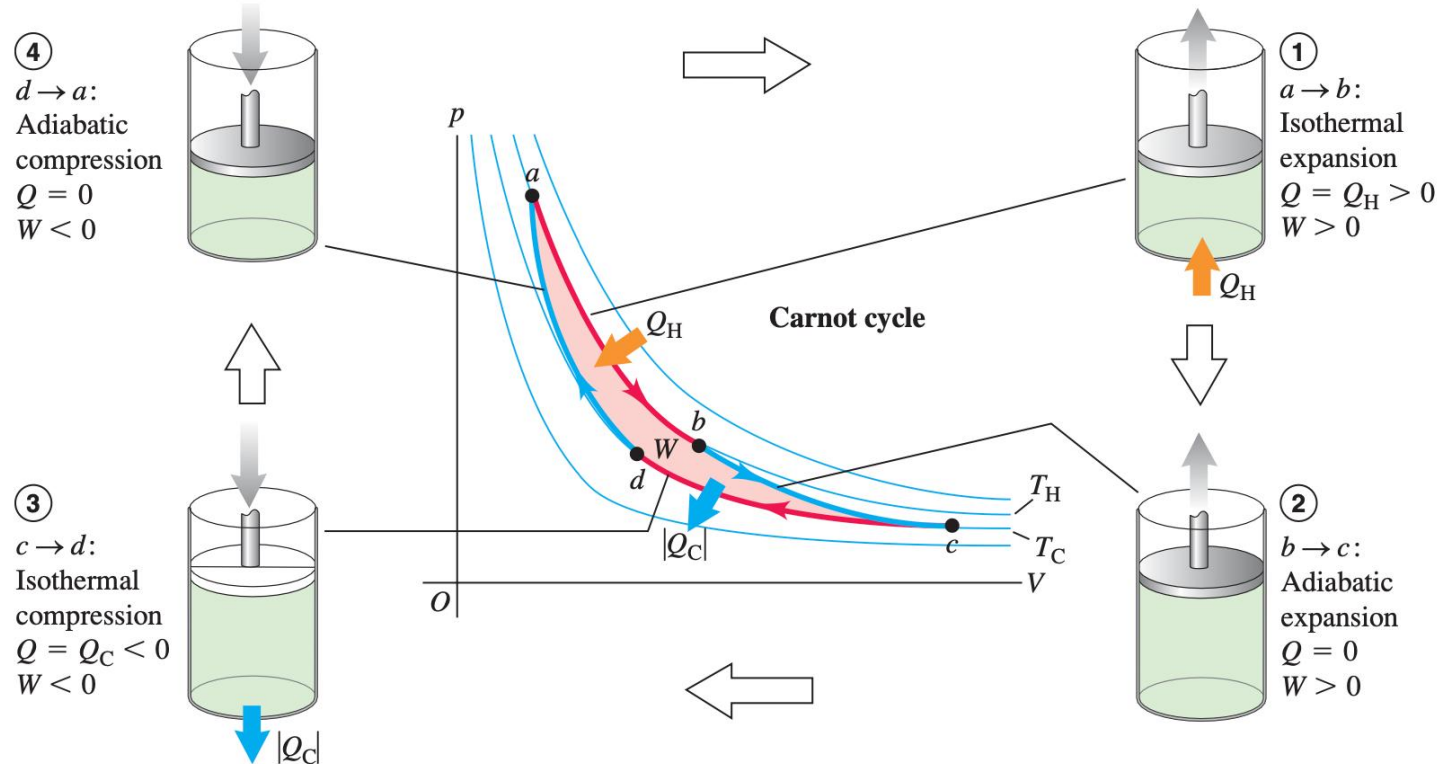
20-6 The Carnot Cycle



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

$$cd: Q_C = W_{cd} = nRT_C \ln \frac{V_d}{V_c} = -nRT_C \ln \frac{V_c}{V_d}$$

20-6 The Carnot Cycle



Adiabatic process da, bc

$$T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1} \quad \text{and} \quad T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1}$$

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}$$

20-6 The Carnot Cycle

Thermal efficiency e of a Carnot engine

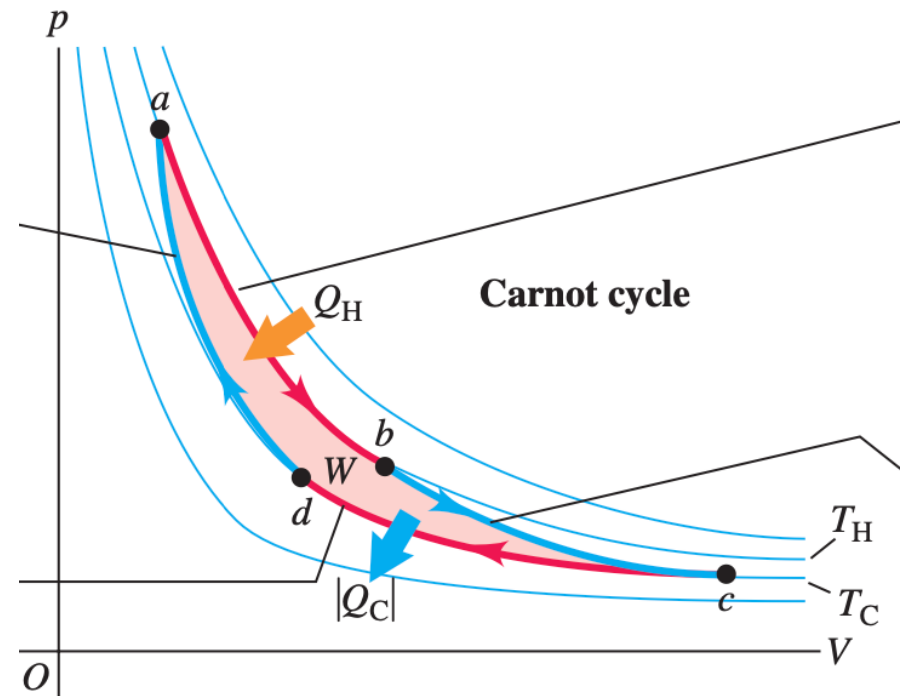
$$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right|$$

$$\frac{Q_C}{Q_H} = - \left(\frac{T_C}{T_H} \right) \frac{\ln(V_c/V_d)}{\ln(V_b/V_a)}$$

because of adiabatic process

$$\frac{Q_C}{Q_H} = - \frac{T_C}{T_H}$$

$$e_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}$$



Sample Problem

Example 20.2 Analyzing a Carnot engine I

A Carnot engine takes 2000 J of heat from a reservoir at 500 K, does some work, and discards some heat to a reservoir at 350 K. How much work does it do, how much heat is discarded, and what is its efficiency?

EXECUTE: From Eq. (20.13),

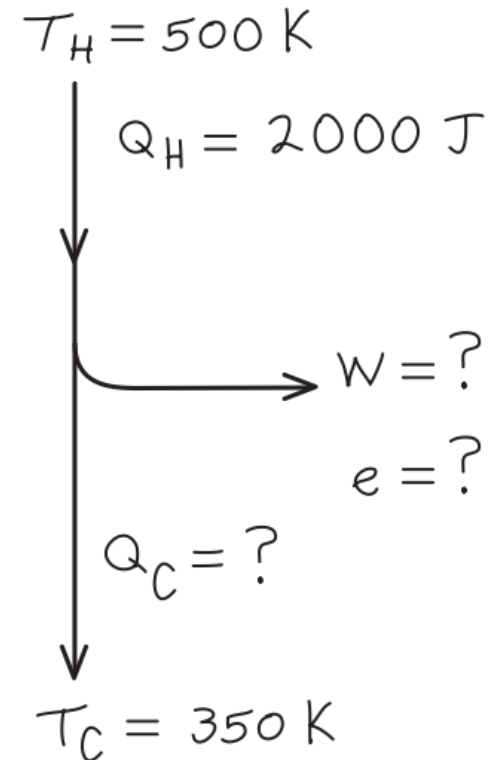
$$Q_C = -Q_H \frac{T_C}{T_H} = -(2000 \text{ J}) \frac{350 \text{ K}}{500 \text{ K}} = -1400 \text{ J}$$

Then from Eq. (20.2), the work done is

$$W = Q_H + Q_C = 2000 \text{ J} + (-1400 \text{ J}) = 600 \text{ J}$$

From Eq. (20.14), the thermal efficiency is

$$e = 1 - \frac{T_C}{T_H} = 1 - \frac{350 \text{ K}}{500 \text{ K}} = 0.30 = 30\%$$



20-6 The Carnot Cycle

The Carnot Refrigerator

Because each step in the Carnot cycle is reversible, the *entire cycle* may be reversed, converting the engine into a refrigerator. The coefficient of performance of the Carnot refrigerator is obtained by combining the general definition of K , Eq. (20.9), with Eq. (20.13) for the Carnot cycle. We first rewrite Eq. (20.9) as

$$K = \frac{|Q_C|}{|Q_H| - |Q_C|} = \frac{|Q_C|/|Q_H|}{1 - |Q_C|/|Q_H|}$$

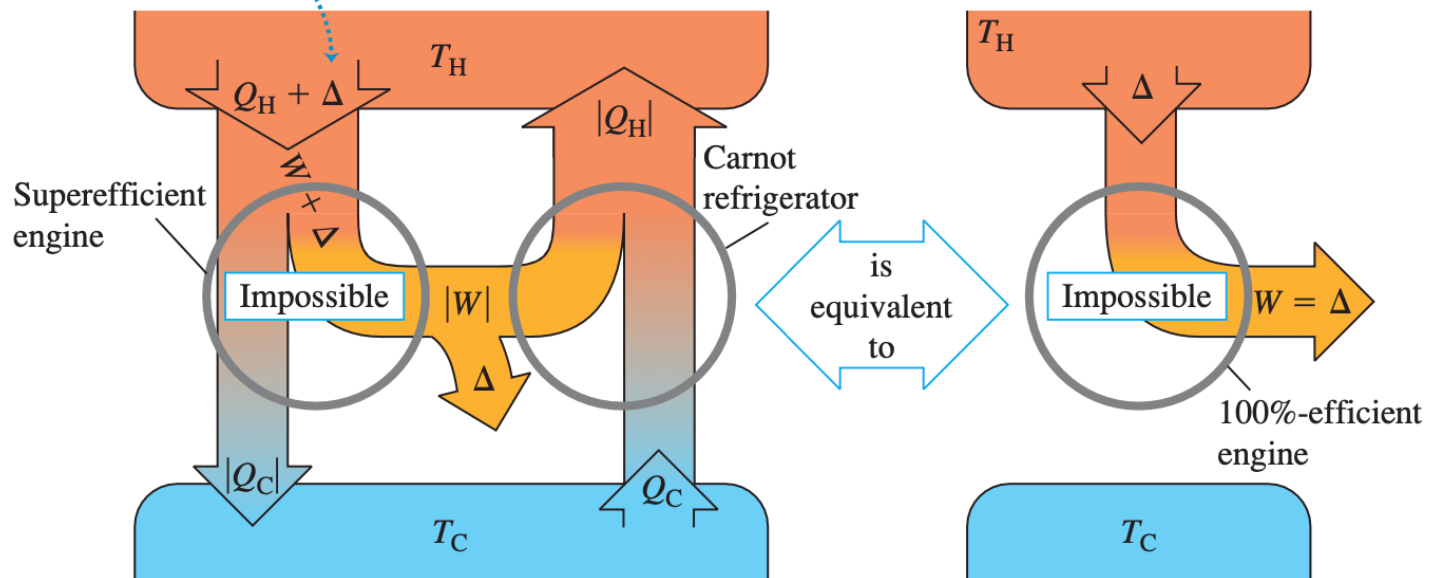
$$K_{\text{Carnot}} = \frac{T_C}{T_H - T_C} \quad (\text{coefficient of performance of a Carnot refrigerator})$$

20-6 The Carnot Cycle

The Carnot Cycle and the Second Law

We can prove that **no engine can be more efficient than a Carnot engine operating between the same two temperatures**. The key to the proof is the above observation that since each step in the Carnot cycle is reversible, the *entire cycle* may be reversed. Run backward, the engine becomes a refrigerator.

If a superefficient engine were possible, it could be used in conjunction with a Carnot refrigerator to convert the heat Δ completely to work, with no net transfer to the cold reservoir.



20-7 Entropy



firecrackers explode,
disorder increases

20-7 Entropy

Entropy provides a *quantitative* measure of disorder.

$$dQ = dW = p dV = \frac{nRT}{V} dV \quad \text{so} \quad \frac{dV}{V} = \frac{dQ}{nRT}$$

Infinitesimal entropy change

$$dS = \frac{dQ}{T} \quad (\text{infinitesimal reversible process})$$

$$\Delta S = S_2 - S_1 = \frac{Q}{T} \quad (\text{reversible isothermal process})$$

Sample Problem

Example 20.5 Entropy change in melting

What is the change of entropy of 1 kg of ice that is melted reversibly at 0°C and converted to water at 0°C? The heat of fusion of water is $L_f = 3.34 \times 10^5 \text{ J/kg}$.

EXECUTE: The heat needed to melt the ice is $Q = mL_f = 3.34 \times 10^5 \text{ J}$. Then from Eq. (20.18),

$$\Delta S = S_2 - S_1 = \frac{Q}{T} = \frac{3.34 \times 10^5 \text{ J}}{273 \text{ K}} = 1.22 \times 10^3 \text{ J/K}$$

20-7 Entropy

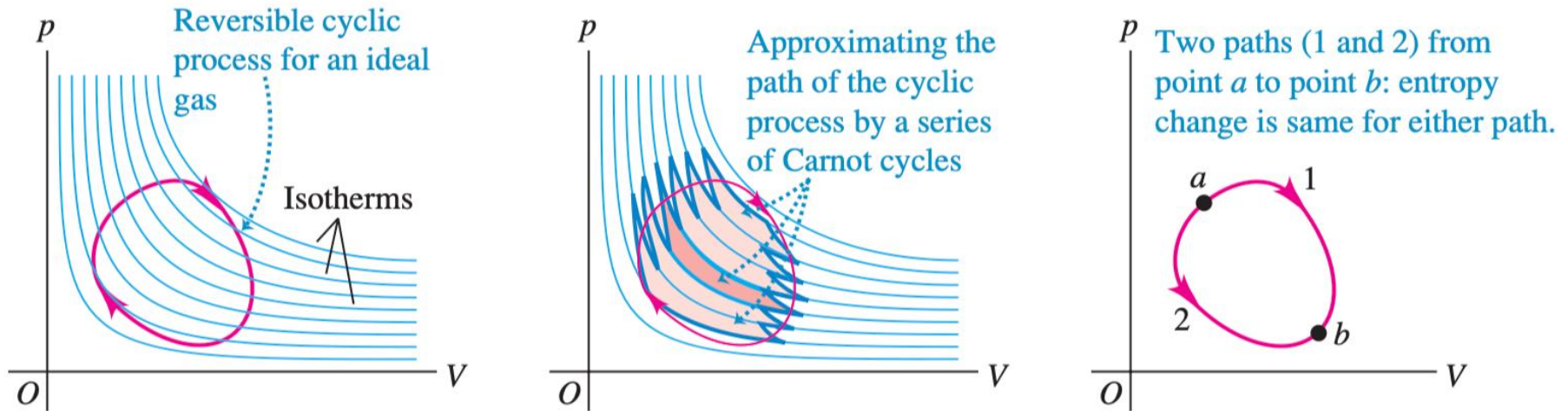
Entropy in Reversible Processes

We can generalize the definition of entropy change to include *any* reversible process leading from one state to another, whether it is isothermal or not. We represent the process as a series of infinitesimal reversible steps. During a typical step, an infinitesimal quantity of heat dQ is added to the system at absolute temperature T . Then we sum (integrate) the quotients dQ/T for the entire process; that is,

$$\Delta S = \int_1^2 \frac{dQ}{T} \quad (\text{entropy change in a reversible process}) \quad (20.19)$$

The limits 1 and 2 refer to the initial and final states.

20-7 Entropy



$$\text{Total entropy change } \Delta S = \frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

Total entropy change during *any* reversible cycle is zero

All *irreversible* processes involve an increase in entropy.
Unlike energy, *entropy is not a conserved quantity*.

20-7 Entropy

Entropy statement of second law:

The entropy of a closed system can never decrease. A closed system can never spontaneously undergo a process that decreases the number of possible microscopic states

Sample Problem

Example 20.6 Entropy change in a temperature change

One kilogram of water at 0°C is heated to 100°C. Compute its change in entropy. Assume that the specific heat of water is constant at 4190 J/kg · K over this temperature range.

EXECUTE: From Eq. (17.14) the heat required to carry out each infinitesimal step is $dQ = mc dT$. Substituting this into Eq. (20.19) and integrating, we find

$$\begin{aligned}\Delta S &= S_2 - S_1 = \int_1^2 \frac{dQ}{T} = \int_{T_1}^{T_2} mc \frac{dT}{T} = mc \ln \frac{T_2}{T_1} \\ &= (1.00 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \left(\ln \frac{373 \text{ K}}{273 \text{ K}} \right) \\ &= 1.31 \times 10^3 \text{ J/K}\end{aligned}$$