Chapter 20

The Second Law of Thermodynamics

PowerPoint® Lectures for
University Physics, 14th Edition
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Learning Goals for Chapter 20

Looking forward at …

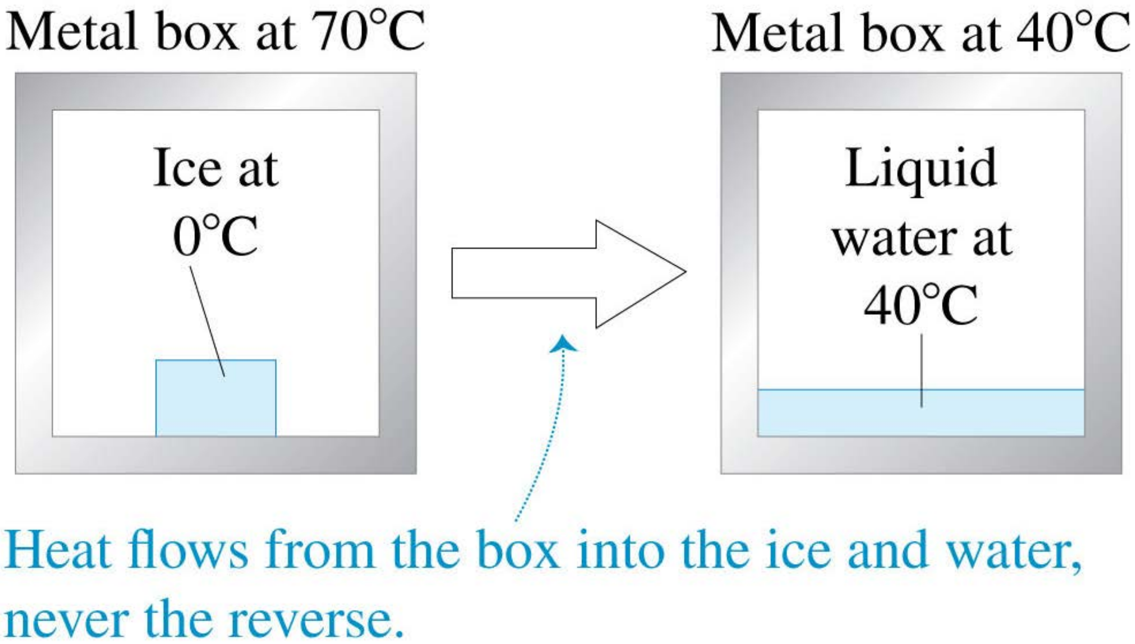
- the difference between reversible and irreversible processes.
- the physics of internal-combustion engines.
- how refrigerators and heat engines are related, and how to analyze the performance of a refrigerator.
- how the second law of thermodynamics sets limits on the efficiency of engines and the performance of refrigerators.
- what is meant by entropy, and how to use this concept to analyze thermodynamic processes.

Introduction

- Why does heat flow from the hot lava into the cooler water?
- Could it flow the other way?
- It is easy to convert mechanical energy completely into heat, but not the reverse. Why not?
- We need to use the second law of thermodynamics and the concept of entropy to answer the above questions.

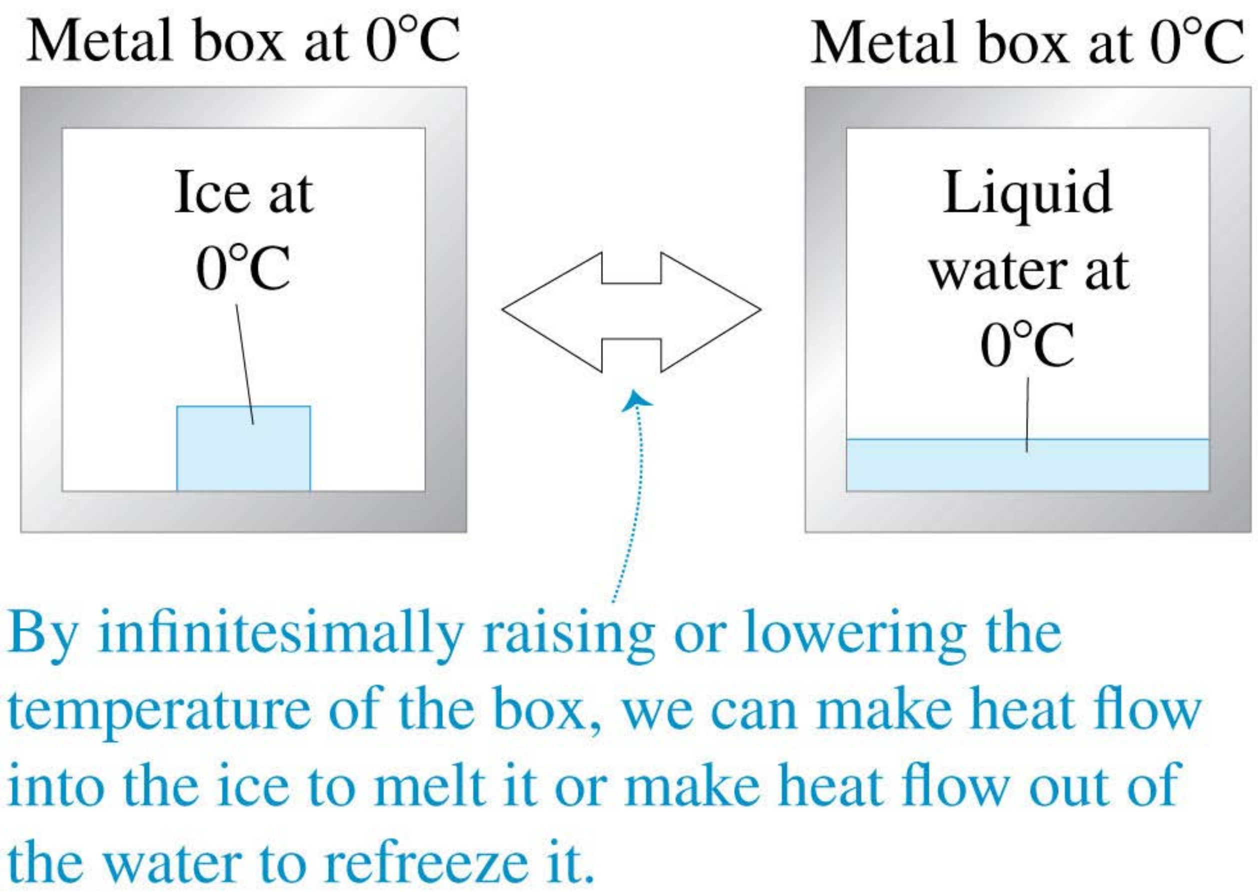
Directions of thermodynamic processes

- The direction of a *reversible process* can be reversed by an infinitesimal change in its conditions.
- The system is always in or very close to thermal equilibrium.
- For example, a block of ice melts *irreversibly* when we place it in a hot metal box.



Directions of thermodynamic processes

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



Q20.1

Which statement about these two thermodynamic processes is *correct?*

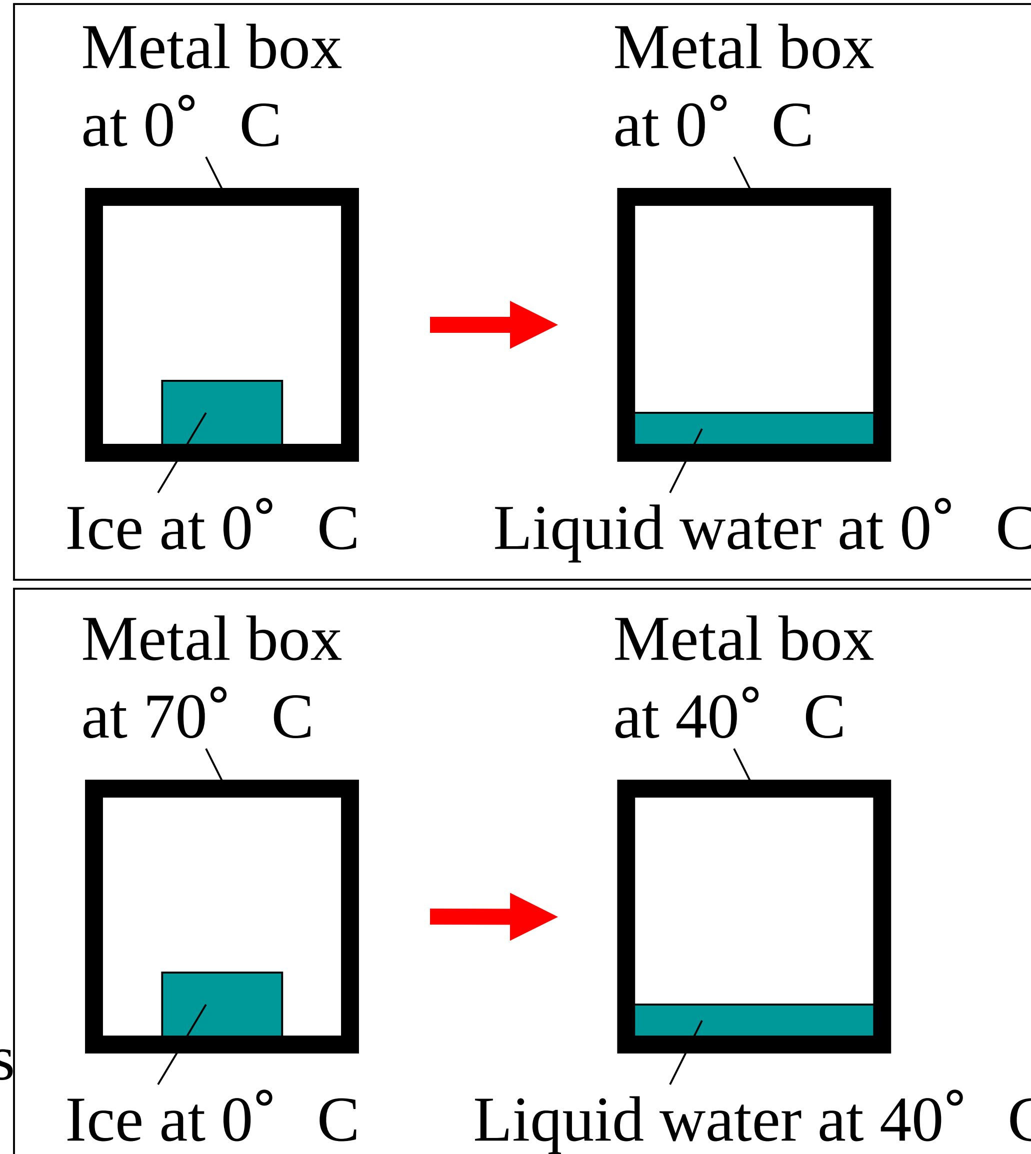
A. Both are reversible.

B. Both are irreversible.

C. The upper one is reversible and the lower one is irreversible.

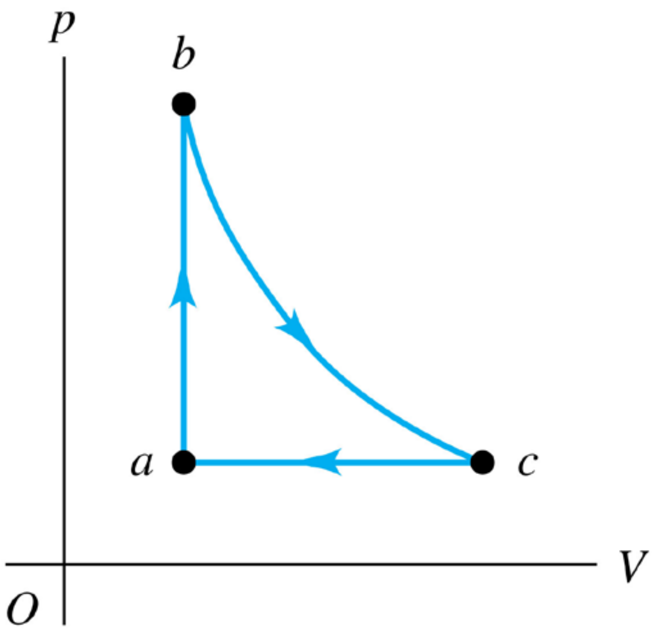
D. The upper one is irreversible and the lower one is reversible.

E. Not enough information is given to decide.



Q20.2

An ideal gas is taken around the cycle shown in this *p*-*V* diagram, from *a* to *b* to *c* and back to *a*. Process $b \rightarrow c$ is *isothermal*. Which of the processes in this cycle could be *reversible*?



A. $a \rightarrow b$

B. $b \rightarrow c$

C. $c \rightarrow a$

D. two or more of A, B, and C

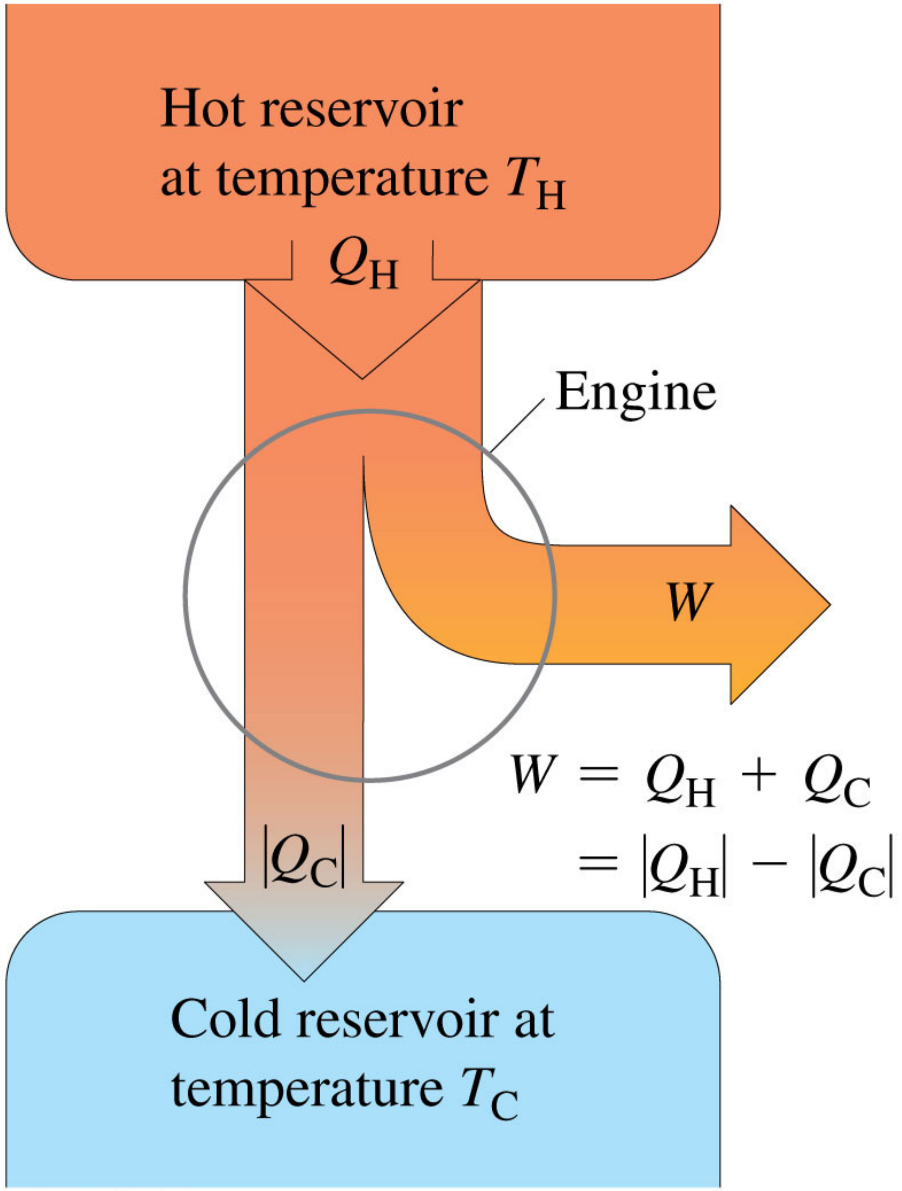
E. none of A, B, or C

Heat engines

- A **heat engine** is any device that partly transforms heat into work or mechanical energy.
- All motorized vehicles other than purely electric vehicles use heat engines for propulsion.
- (Hybrid vehicles use their internal-combustion engine to help charge the batteries for the electric motor.)

Heat engines

- Simple heat engines operate on a *cyclic process* during which they absorb heat Q_H from a hot reservoir and discard some heat Q_C to a cold reservoir.
- Shown is a schematic energy-flow diagram for a heat engine.



The efficiency of a heat engine

- The **thermal efficiency** ***e*** of a heat engine is the fraction of Q_H that is converted to work.

Work done by engine Heat rejected by engine

Thermal efficiency of an engine

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

Heat absorbed by engine

- *e* is what you get divided by what you pay for.
- This is always less than unity, an all-too-familiar experience!

Q20.4

During one cycle, an automobile engine takes in 12,000 J of heat and discards 9000 J of heat. What is the efficiency of this engine?

A. 400%

B. 133%

C. 75%

D. 33%

E. 25%

Q20.5

During one cycle, an automobile engine with an efficiency of 20% takes in 10,000 J of heat. How much work does the engine do per cycle?

A. 8000 J

B. 6400 J

C. 2000 J

D. 1600 J

E. 400 J

Q-RT20.1

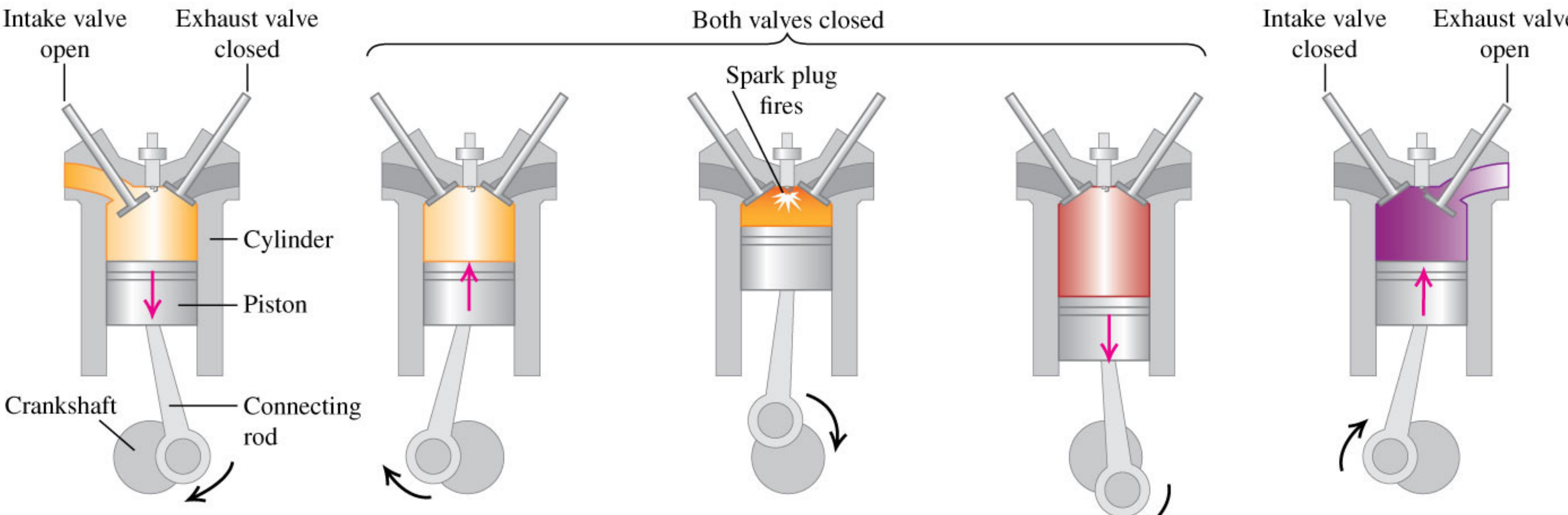
Rank the following heat engines in order from highest to lowest thermal efficiency.

A. An engine that in one cycle absorbs 2500 J of heat and rejects 2250 J of heat

B. An engine that in one cycle absorbs 50,000 J of heat and does 4000 J of work

C. An engine that in one cycle does 800 J of work and rejects 5600 J of heat

Internal-combustion engines



① **Intake stroke:** Piston moves down, causing a partial vacuum in cylinder; gasoline–air mixture enters through intake valve.

② **Compression stroke:** Intake valve closes; mixture is compressed as piston moves up.

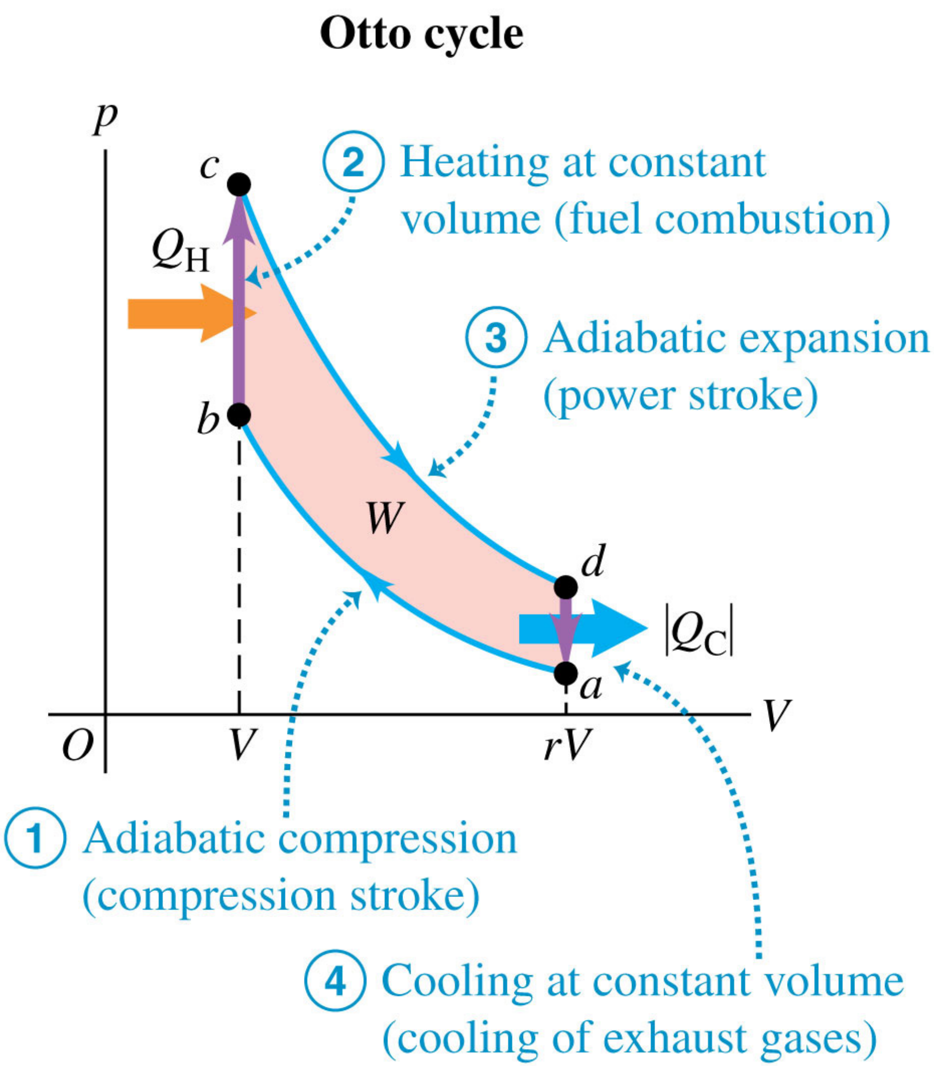
③ **Ignition:** Spark plug ignites mixture.

④ **Power stroke:** Hot burned mixture expands, pushing piston down.

⑤ **Exhaust stroke:** Exhaust valve opens; piston moves up, expelling exhaust and leaving cylinder ready for next intake stroke.

pV-diagram of the Otto cycle

- Along *ab* the gasoline–air mixture is compressed adiabatically 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.



Thermal efficiency in Otto cycle

- The heats $Q_H = nC_V(T_c - T_b) > 0; Q_C = nC_V(T_a - T_d) < 0$

$$e = \frac{W}{Q_H} = \frac{Q_H + Q_C}{Q_H} = \frac{T_c - T_b + T_a - T_d}{T_c - T_b}$$

- Adiabatic processes $T_a(rV)^{\gamma-1} = T_b V^{\gamma-1}; T_d(rV)^{\gamma-1} = T_c V^{\gamma-1}$

where the quantity r is called the compression ratio, typically 8 to 10 for auto engines.

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

Thermal efficiency in Otto cycle

$$e = 1 - \frac{1}{r^{\gamma-1}}$$

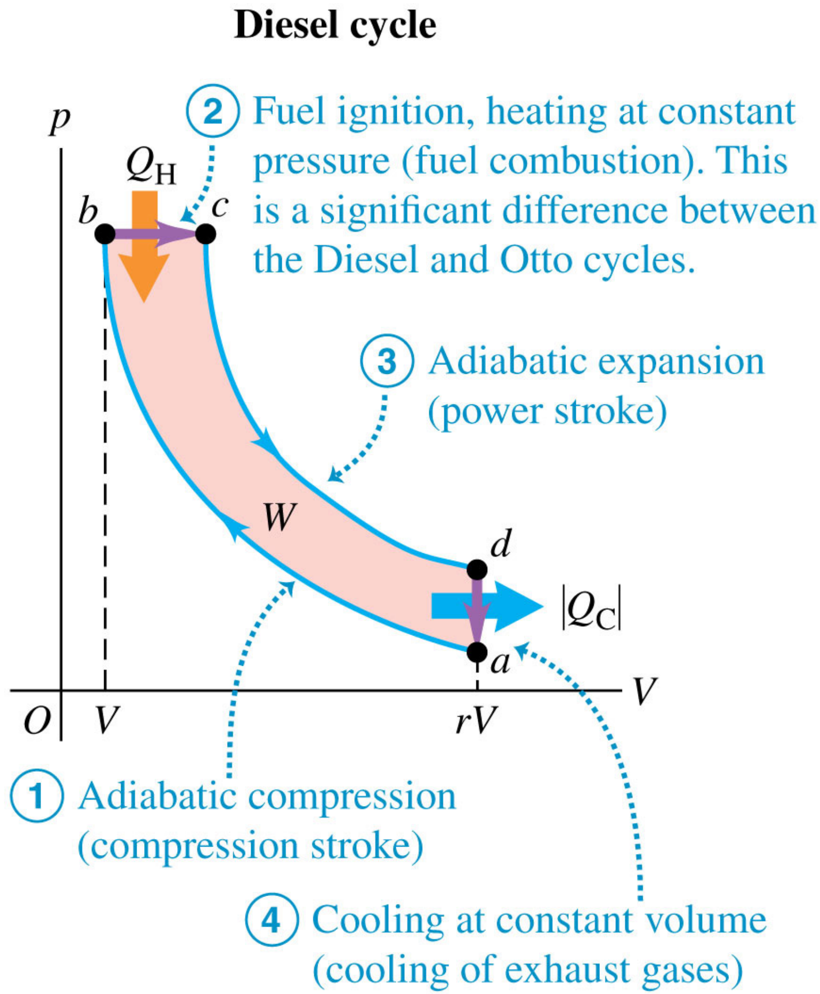
Compression ratio

Ratio of heat capacities

- For air, $\gamma = 1.4$, with $r = 8$ (10), $e = 56\%$ (60%) (highly idealized model! Assume ideal gas, ignores friction, turbulence, lost of heat to walls, etc. Real gasoline engine $e \sim 35\%$.

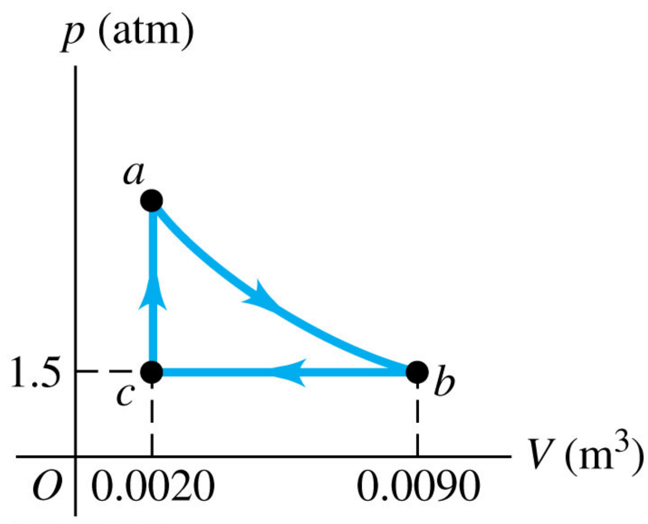
pV-diagram of the Diesel cycle

- Starting at point *a*, air is compressed adiabatically to point *b*, heated at constant pressure to point *c*, expanded adiabatically to point *d*, and cooled at constant volume to point *a*.
- Because there is no fuel in the cylinder during the compression stroke, pre-ignition cannot occur, and the compression ratio *r* (15~20) can be much higher than for a gasoline engine.
- This improves efficiency (66%~70%).



Exercises

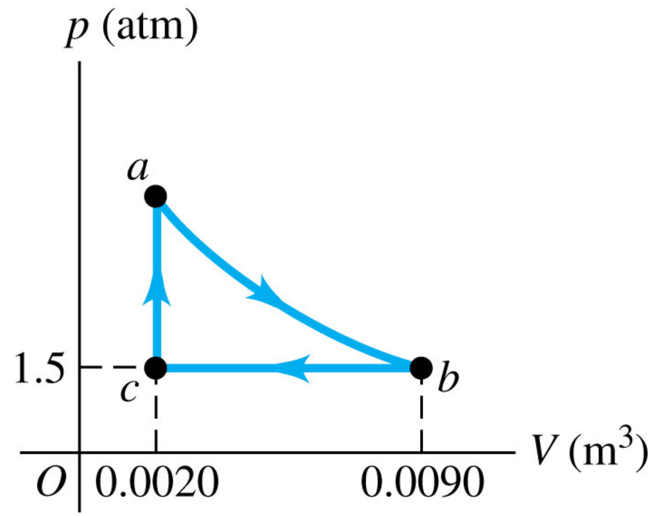
- The *pV*-diagram shows a cycle of a heat engine that uses 0.250 mole of an ideal gas with γ =1.4. Process *ab* is adiabatic. (a) Find the pressure of the gas at point *a*. (b) How much heat enters this gas per cycle, and where does it happen? (c) How much heat leaves this gas in a cycle, and where does it occur? (d) How much work does this engine do in a cycle? (e) What is the thermal efficiency of the engine?



- The Otto-cycle engine in a Mercedes-Benz SLK230 has a compression ratio of 8.8. (a) What is the ideal efficiency of the engine? Use γ =1.4. (b) The engine in a Dodge Viper GT2 has a slightly higher compression ratio of 9.6. How much increase in the ideal efficiency results from this increase in the compression ratio?

Exercises (hints & answers)

- The pV-diagram shows a cycle of a heat engine that uses 0.250 mole of an ideal gas with γ =1.4. Process *ab* is adiabatic. (a) Find the pressure of the gas at point *a*. (b) How much heat enters this gas per cycle, and where does it happen? (c) How much heat leaves this gas in a cycle, and where does it occur? (d) How much work does this engine do in a cycle? (e) What is the thermal efficiency of the engine?



$$C_V = \frac{5}{2}R; C_p = \frac{7}{2}R; p_a V_a^{\gamma} = p_b V_b^{\gamma}$$

$$\text{constant volume}, W = 0, \Delta U = Q = nC_V \Delta T; \text{ideal gas } PV = nRT \Rightarrow n\Delta T = \frac{V\Delta p}{R} \Rightarrow Q = C_V \frac{V\Delta p}{R}$$

$$\text{constant pressure}, W = p\Delta V, Q = nC_P \Delta T; \text{ideal gas } PV = nRT \Rightarrow n\Delta T = \frac{p\Delta V}{R} \Rightarrow Q = C_P \frac{p\Delta V}{R}$$

(12.3 atm; 5470J; -3723J;1747J; 31.9%)

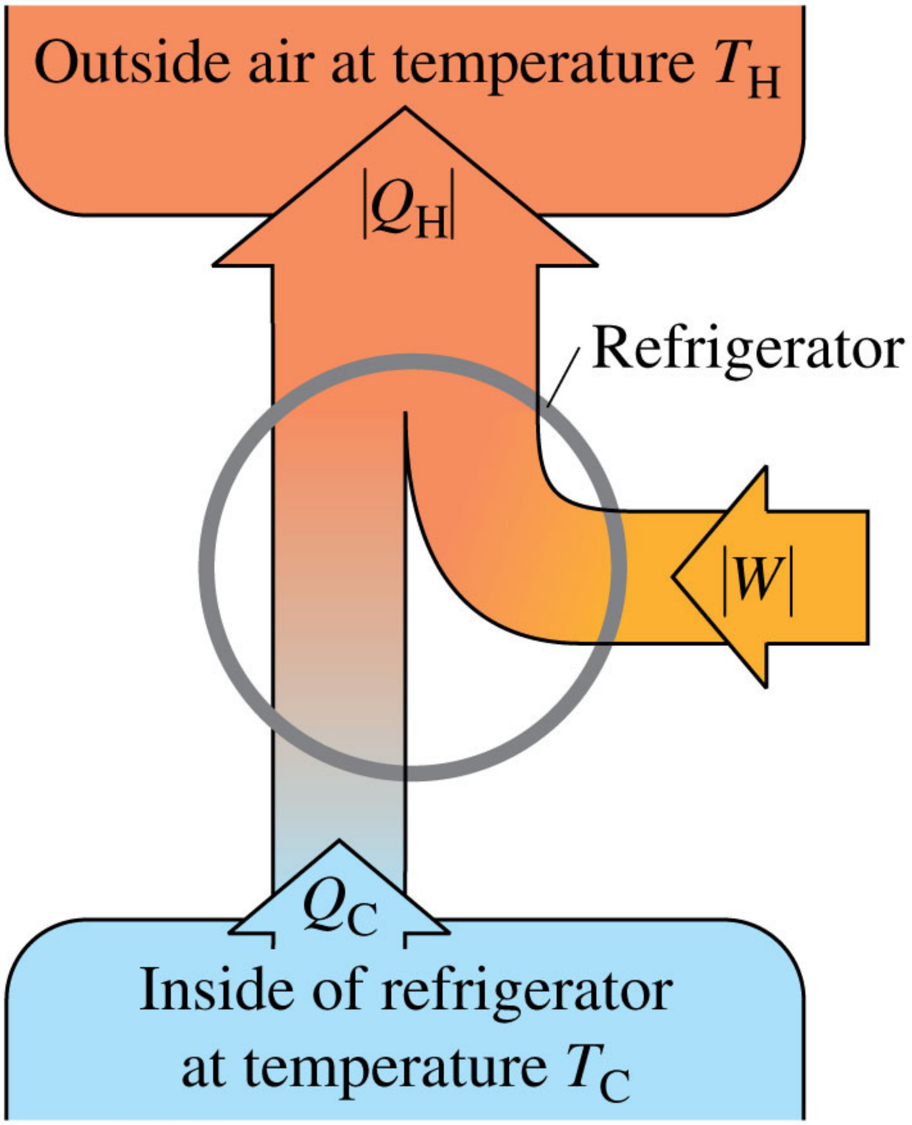
- The Otto-cycle engine in a Mercedes-Benz SLK230 has a compression ratio of 8.8. (a) What is the ideal efficiency of the engine? Use γ =1.4. (b) The engine in a Dodge Viper GT2 has a slightly higher compression ratio of 9.6. How much increase in the ideal efficiency results from this increase in the compression ratio?

(58.1%, 59.5%)

$$e = 1 - \frac{1}{r^{\gamma-1}}$$

Refrigerators

- A **refrigerator** takes heat from a cold place (inside the refrigerator) and gives it off to a warmer place (the room). An *input* of mechanical work is required to do this.
- A refrigerator is essentially a heat engine operating in reverse.
- Shown is an energy-flow diagram of a refrigerator.



Refrigerators: Coefficient of performance

- From an economic point of view, the best refrigeration cycle is one that removes the greatest amount of heat from the inside of the refrigerator for the least expenditure of mechanical work.
- The relevant ratio is therefore $|Q_C|/|W|$; the larger this ratio, the better the refrigerator.
- We call this ratio the coefficient of performance, K:

Coefficient of performance of a refrigerator

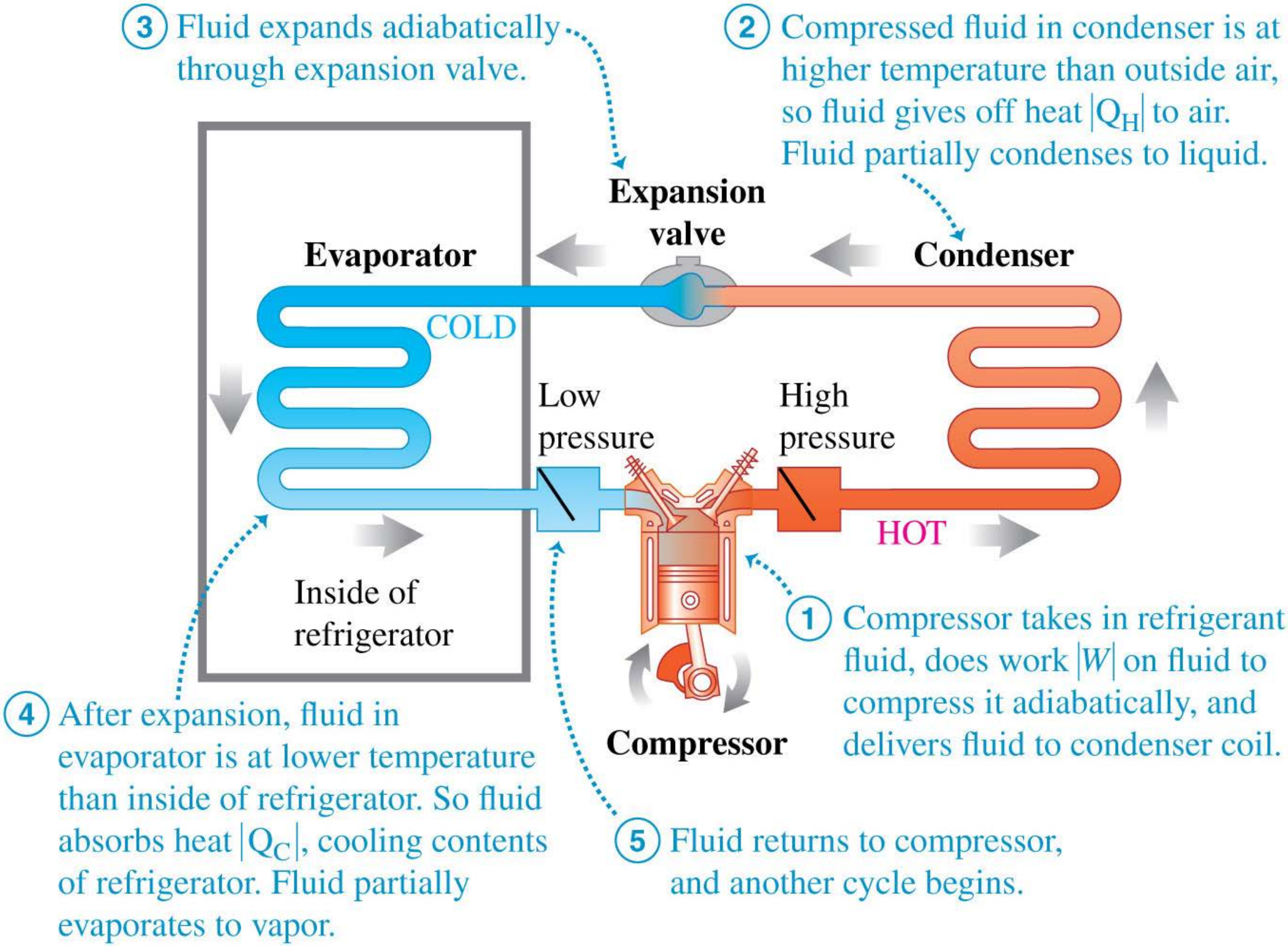
$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|}$$

Heat removed from inside of refrigerator

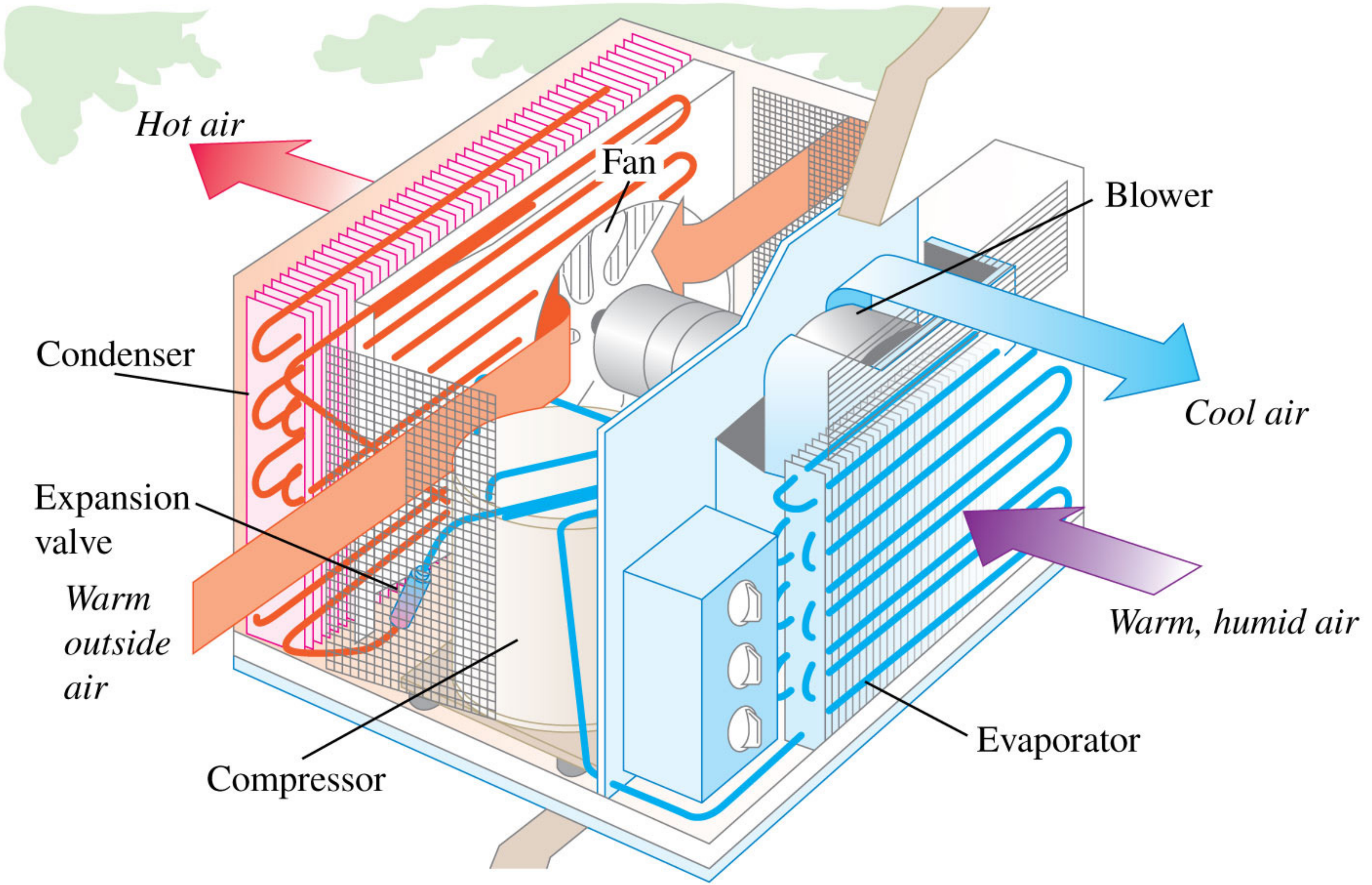
Work input of refrigerator

Heat rejected to outside air

Principle of the mechanical refrigeration cycle



Air conditioner



Exercises

- A refrigerator has a coefficient of performance of 2.10. In each cycle it absorbs 3.10×10^4 J of heat from the cold reservoir. (a) How much mechanical energy is required each cycle to operate the refrigerator? (b) During each cycle, how much heat is discarded to the high-temperature reservoir?

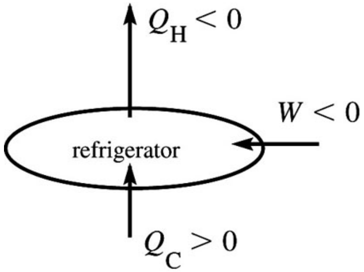
- A refrigerator has a coefficient of performance of 2.25, runs on an input of 135 W of electric power, and keeps its inside compartment at 5℃. If you put a dozen 1.0-L plastic bottles of water at 31℃ into this refrigerator, how long will it take for them to be cooled down to 5℃? (Ignore any heat leaves the plastic. The specific heat of water is 4190 J/kg · ℃. The mass density of water is 1000 kg/m^3.)

Exercises (hints & answers)

- A refrigerator has a coefficient of performance of 2.10. In each cycle it absorbs 3.10 × 10^4 J of heat from the cold reservoir. (a) How much mechanical energy is required each cycle to operate the refrigerator? (b) During each cycle, how much heat is discarded to the high-temperature reservoir?

$$K = \frac{|Q_C|}{|W|}; W = Q_C + Q_H$$

(1.48 × 10^4 J;-4.58 × 10^4 J)



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$$Q = mc\Delta T; P = \frac{|W|}{t}; K = \frac{|Q_C|}{|W|}$$

(71.88 min)

The second law of thermodynamics

- The *second law of thermodynamics* can be stated in several ways:

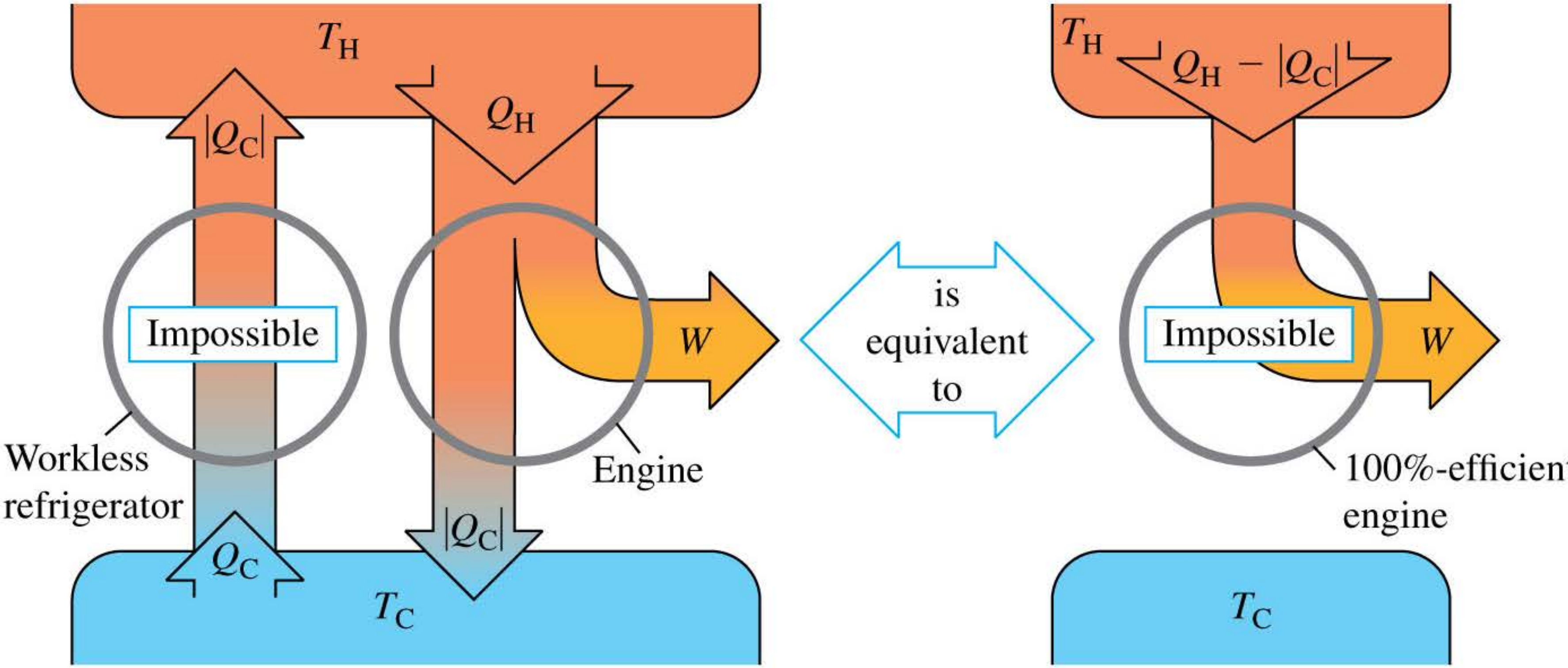
✓**It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began.**

- We will call this the "engine" statement of the second law.

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

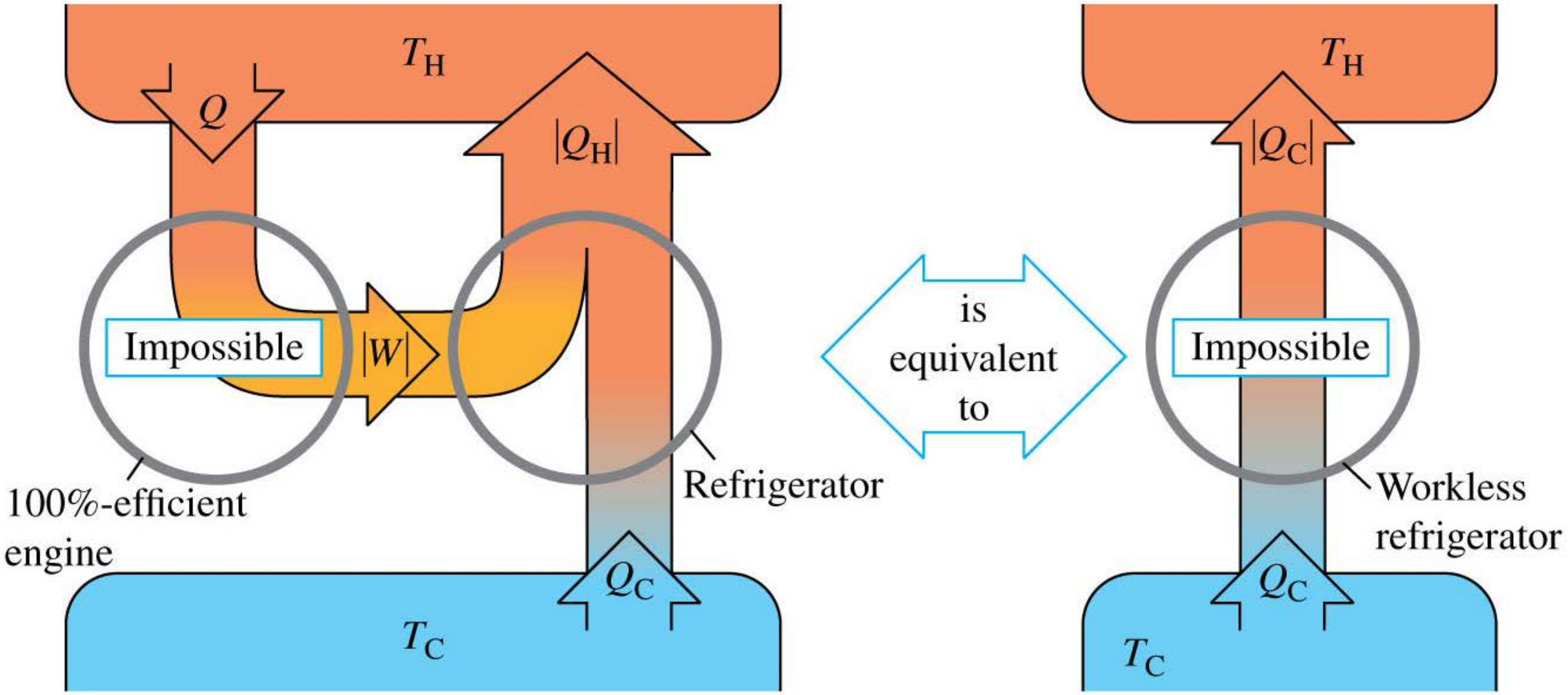
- We'll call this the "refrigerator" statement of the second law.

The second law of thermodynamics



- 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.

The second law of thermodynamics



- 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.

Q20.6

A copper pot at room temperature is filled with room-temperature water. Imagine a process whereby the water spontaneously freezes and the pot becomes hot. Why is such a process impossible?

A. It violates the first law of thermodynamics.

B. It violates the second law of thermodynamics.

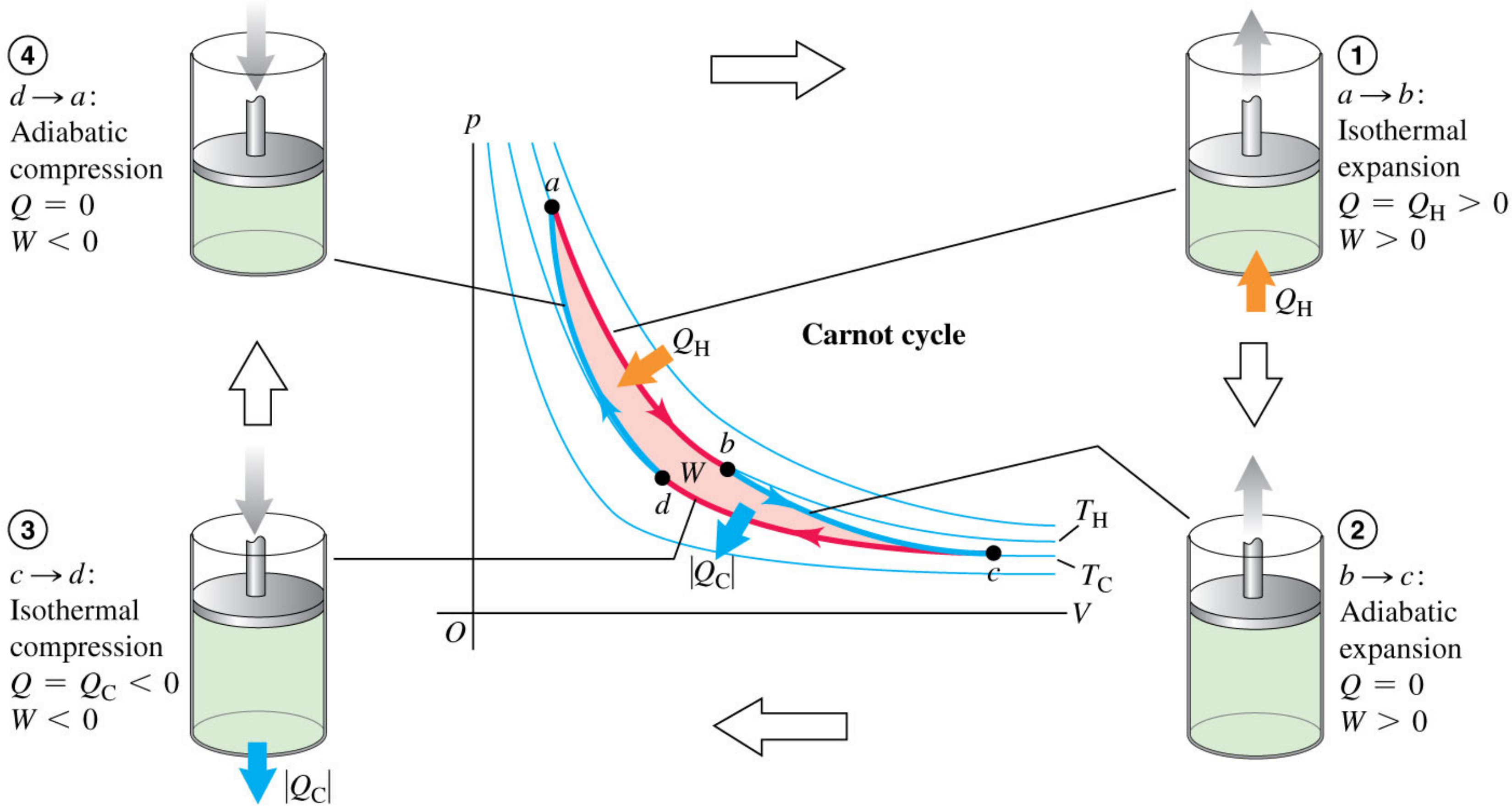
C. It violates both the first and second laws of thermodynamics.

D. It violates the law of conservation of energy.

E. none of the above

The Carnot cycle

- No heat engine can have 100% efficiency. Given two heat reservoirs, how great an efficiency can an engine have? Answered in 1824 by the French Engineer Sadi Carnot. A *Carnot cycle* has two adiabatic segments and two isothermal segments.



The Carnot engine

- The Carnot cycle consists of the following steps:
  1. The gas expands isothermally at temperature T_H, absorbing heat Q_H.
  2. It expands adiabatically until its temperature drops to T_C.
  3. It is compressed isothermally at T_C, rejecting heat $|Q_C|$.
  4. It is compressed adiabatically back to its initial state at temperature T_H.

The efficiency of a Carnot engine

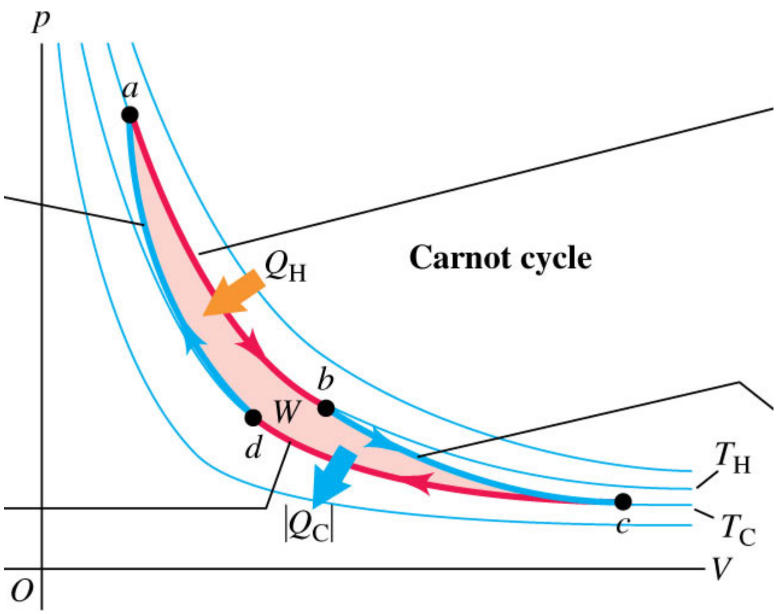
$$Q_H = W_{ab} = nRT_H \ln\frac{V_b}{V_a}; Q_C = W_{cd} = nRT_C \ln\frac{V_d}{V_c} = -nRT_C \ln\frac{V_c}{V_d}$$

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

$$T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}; T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1}$$

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

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



- The efficiency of a Carnot engine is:

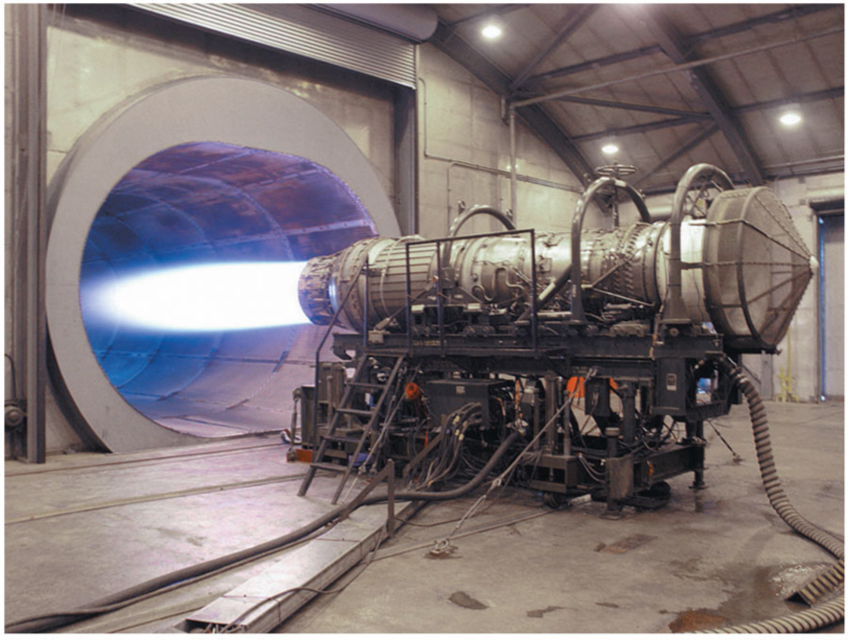
$$\underbrace{e_{\text{Carnot}}}_{\text{Efficiency of a Carnot engine}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}$$

Temperature of cold reservoir

Temperature of hot reservoir

Engine efficiency

- To maximize the efficiency of a real engine, the designer must make the intake temperature T_H as high as possible and the exhaust temperature T_C as low as possible.
- For this reason, the temperatures inside a jet engine are made as high as possible.



- Exotic ceramic materials are used that can withstand temperatures in excess of 1000°C without melting or becoming soft.

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:

Coefficient of performance of a Carnot refrigerator

$$K_{\text{Carnot}} = \frac{T_{\text{C}}}{T_{\text{H}} - T_{\text{C}}}$$

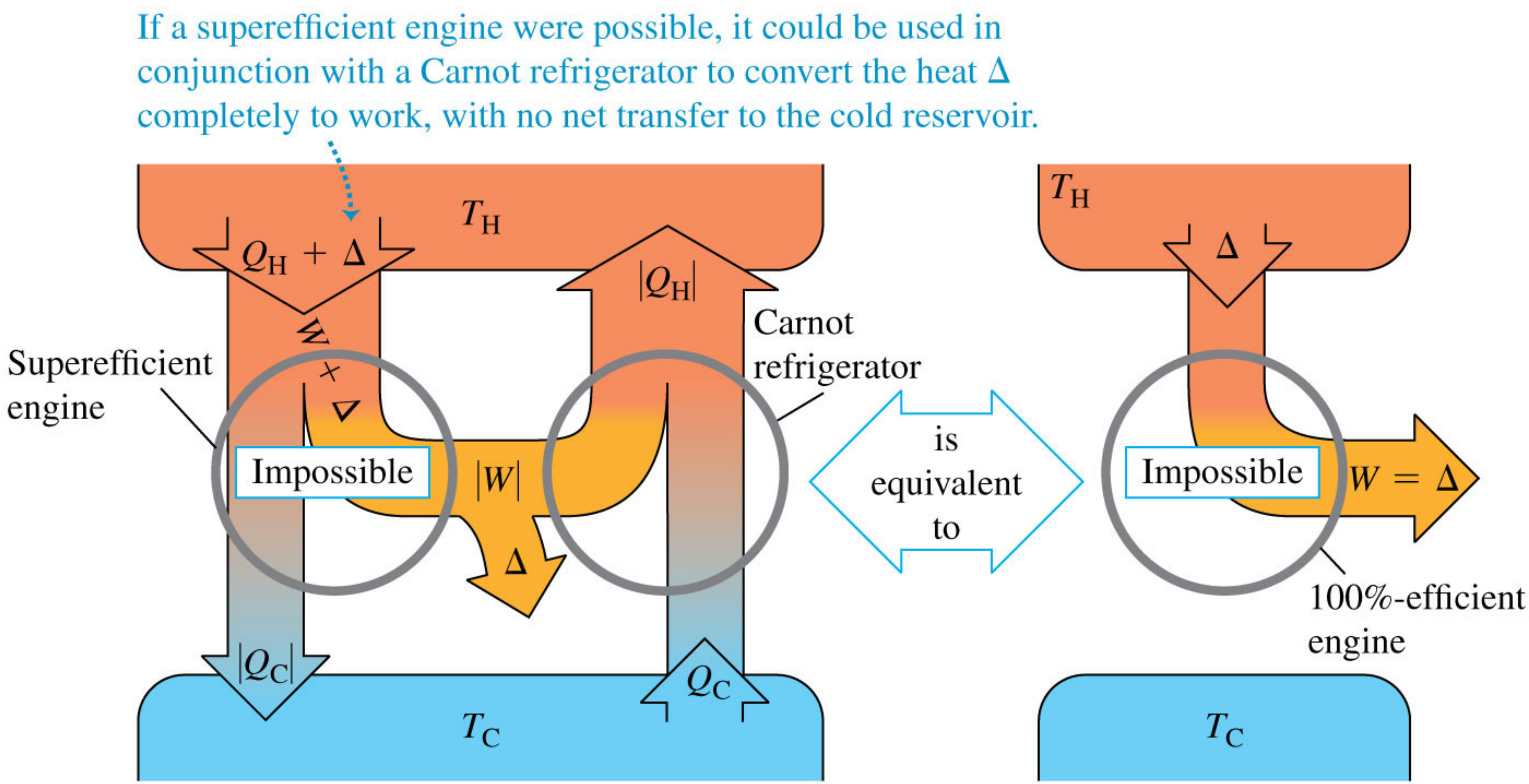
Temperature of cold reservoir

Temperature of hot reservoir

$$\text{derived from}: K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|} = \frac{|Q_C / Q_H|}{1 - |Q_C / Q_H|}; \frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H}$$

The Carnot cycle and the second law

- No engine can be more efficient than a Carnot engine operating between the same two temperatures.



Q20.7

A Carnot engine takes heat in from a reservoir at 400 K and discards heat to a reservoir at 300 K. If the engine does 12,000 J of work per cycle, how much heat does it take in per cycle?

A. 48,000 J

B. 24,000 J

C. 16,000 J

D. 9000 J

E. none of the above

Exercises

- 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?

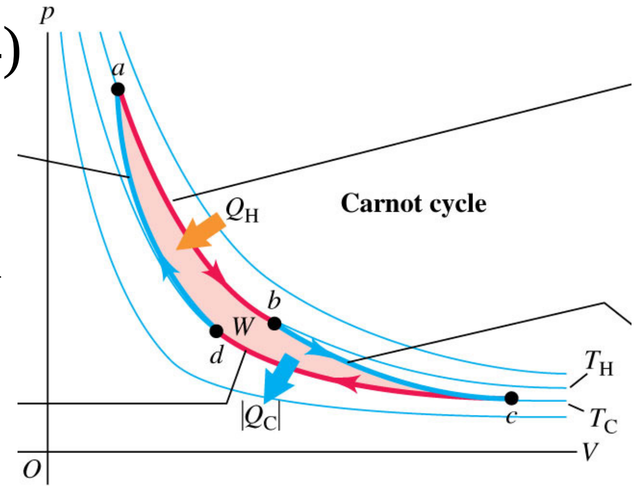
Exercises (hints & answers)

- 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?

$$e_{Carnot} = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H} = \frac{W}{Q_H} = \frac{Q_H + Q_C}{Q_H}$$

(600J, -1400J; 30%)

Exercises

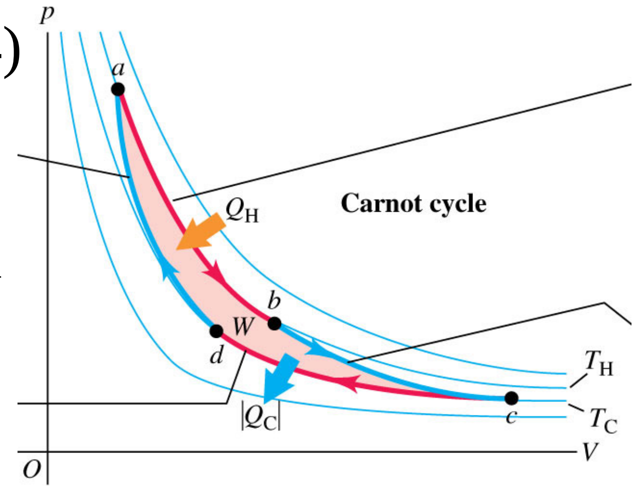


- Suppose 0.200 mole of an ideal diatomic gas (γ=1.4) undergoes a Carnot cycle between 227℃ and 27℃, starting at $p_a = 10.0 \times 10^5$ Pa at point *a* in the *pV*-diagram. The volume doubles during the isothermal expansion step *a* to *b*. (a) Find the pressure and volume at points *a*,*b*,*c*,*d*. (b)Find *Q*, *W* and *ΔU* for each step and for the entire cycle. (c)Find the efficiency directly from the results of part (b), and compare with the value calculate from the equation of efficiency.

- If the cycle described in the above exercise is run backward as a refrigerator, what is its coefficient of performance?

Exercises (hints & answers)

- Suppose 0.200 mole of an ideal diatomic gas (γ=1.4) undergoes a Carnot cycle between 227℃ and 27℃, starting at p_a=10.0 × 10^5 Pa at point *a* in the *pV*-diagram. The volume doubles during the isothermal expansion step *a* to *b*. (a) Find the pressure and volume at points *a,b,c,d*. (b)Find *Q*, *W* and *ΔU* for each step and for the entire cycle. (c)Find the efficiency directly from the results of part (b), and compare with the value calculate from the equation of efficiency.



$$pV = nRT; TV^{\gamma-1} = \text{const.(adiabatic)}; \Delta U = Q\text{-}W = nC_V \Delta T; W_{isothermal} = nRT \ln\frac{V_2}{V_1}; e = \frac{W}{Q_H} = \frac{T_H - T_C}{T_H}$$

(10.0 × 10^5 Pa; 5.0 × 10^5 Pa; 0.837 × 10^5 Pa; 1.67 × 10^5 Pa; 8.31 × 10^{-4}m^3; 16.6 × 10^{-4}m^3; 59.6 × 10^{-4}m^3; 29.8 × 10^{-4}m^3; *ab*:576J, 576J, 0; *bc*:0, 832J, -832J;*cd*:-346J, -346J, 0; *da*:0 -832J, 832J; 40%)

- If the cycle described in the above exercise is run backward as a refrigerator, what is its coefficient of performance?

(1.5)

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

Entropy and disorder

- The 2nd law of thermodynamics as previously stated is not an equation or a quantitative relationship but rather a statement of impossibility. However, the law can be stated as a quantitative relationship using the concept of entropy.
- *Entropy* provides a *quantitative* measure of disorder.
- Many processes proceed naturally in the direction of increasing randomness.
- Adding heat to a body increases average molecular speeds; therefore, molecular motion becomes more random.
- The explosion of the firecracker shown increases its disorder and entropy.

Entropy in reversible processes

- We introduce the symbol S for the entropy of the system, and we define the infinitesimal entropy change dS during an infinitesimal reversible process at absolute temperature T as:

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

- The total entropy change over any reversible process is:

Entropy change in a reversible process

$$\Delta S = \int_1^2 \frac{dQ}{T}$$

Upper limit = final state

Infinitesimal heat flow into system

Lower limit = initial state

Absolute temperature

- Since entropy is a measure of the randomness of a system in any specific state, it must depend only on the current state of the system, not on its past history. $\Delta S=S_2-S_1$, only depends on states 1 and 2, not only the path leading from state 1 to state 2.

Exercises

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

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

Exercises (hints and answers)

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

$$Q = mL_f ; \Delta S = \frac{Q}{T}$$

(1.22×10^3 J/K)

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

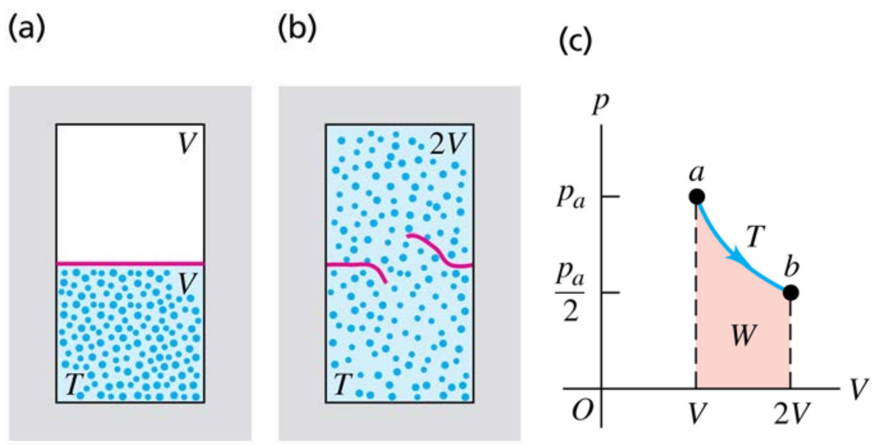
$$\Delta S = \int_1^2 \frac{dQ}{T} = \int_1^2 \frac{mcdT}{T} = mc \ln \frac{T_2}{T_1}$$

(1.31×10^3 J/K)

Exercises

- A gas expands adiabatically and reversibly. What is the change in entropy?

- A partition divides a thermally insulated box into two compartments, each of volume V. Initially, one compartment contains n moles of an ideal gas at temperature T, and the other compartment is evacuated. We break the partition and the gas expands, filling both compartments. What is the entropy change in this free-expansion process?



In such free-expansion process, Q=0, W=0,ΔU=0, thus entropy change ΔS=Q/T=0? Reversible or irreversible?

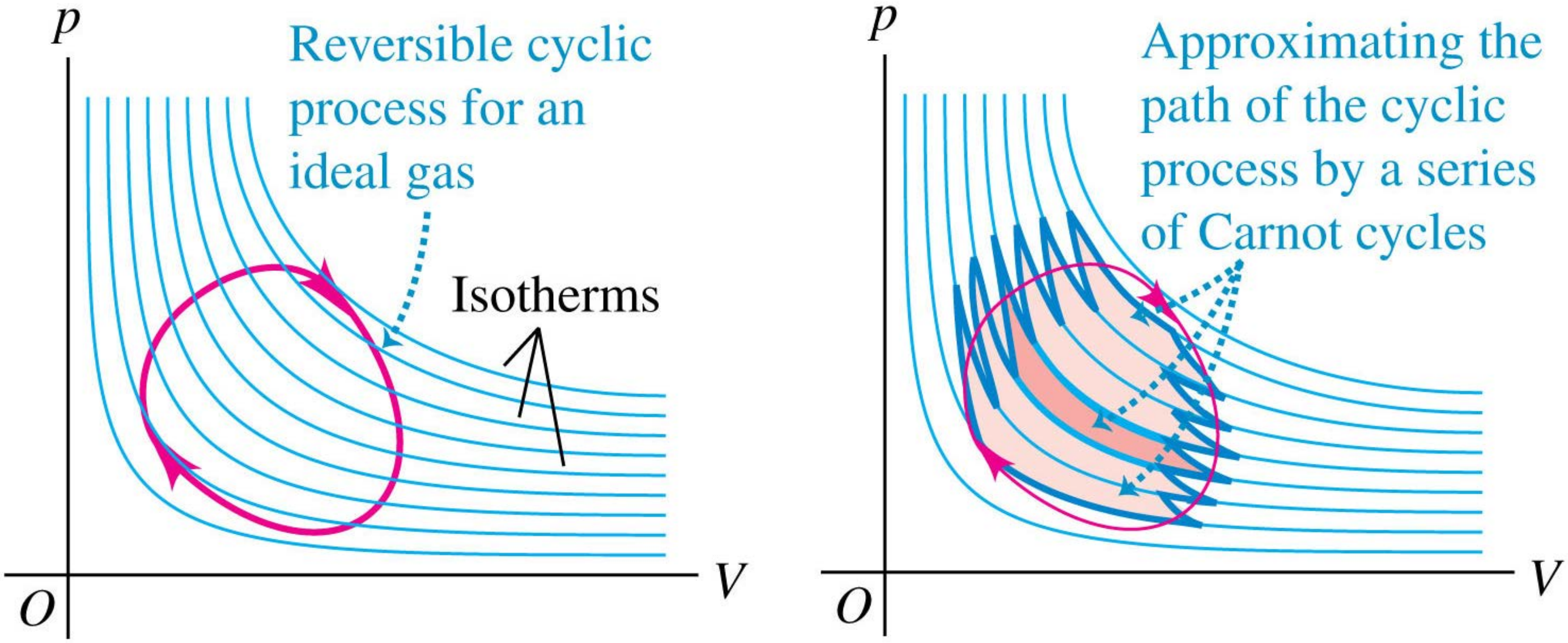
(nRln2)

Entropy in cyclic processes

- The total entropy change in one cycle of any Carnot engine is zero.

$$\left(\text{since}\ \frac{Q_C}{Q_H} = -\frac{T_C}{T_H} \Rightarrow \frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0, i.e.\Delta S_H + \Delta S_C = 0\right)$$

- This result can be generalized to show that the total entropy change during *any* reversible cyclic process is zero.



Exercises

- Suppose 1.00 kg of water at 100℃ is placed in thermal contact with 1.00 kg of water at 0℃. What is the total change in entropy? Assume that the specific heat of water is constant at 4190 J/kg·K over this temperature range.

Exercises (hints and answers)

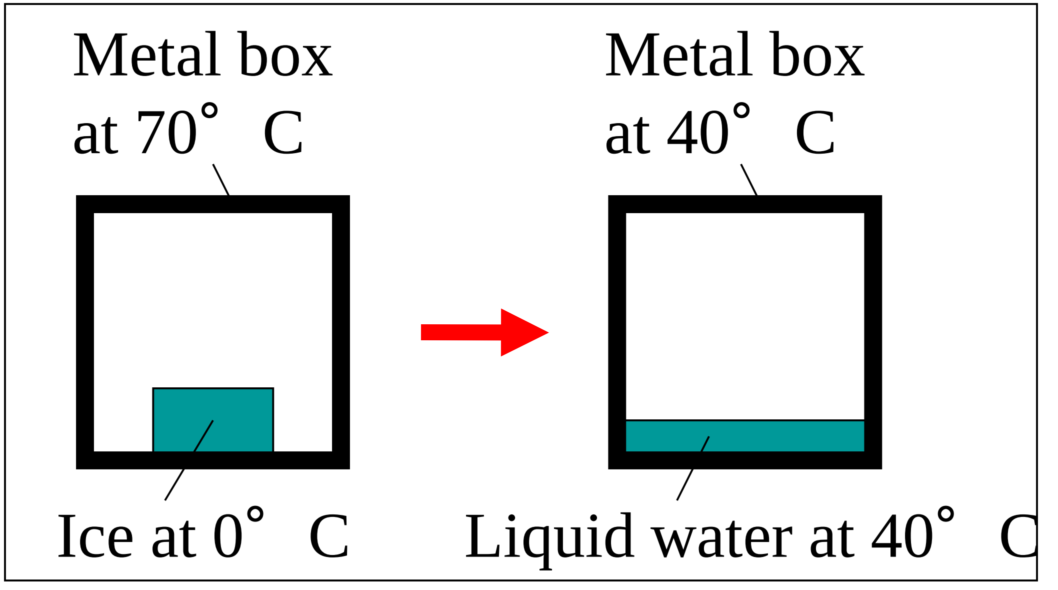
- Suppose 1.00 kg of water at 100 ℃ is placed in thermal contact with 1.00 kg of water at 0 ℃. What is the total change in entropy? Assume that the specific heat of water is constant at 4190 J/kg·K over this temperature range.

$$\Delta S = mc\int_{T_1}^{T_2}\frac{dT}{T}$$

$$(\Delta S_H = -603\text{J/K}; \Delta S_C = +705\text{J/K}; \Delta S_{total} = +102\text{J/K})$$

Q20.8

You put an ice cube at 0° C inside a large metal box at 70° C. The ice melts and the entropy of the ice increases. Which statement is correct?



A. Entropy of the metal box is unchanged; total entropy increases.

B. Entropy of the metal box decreases; total entropy decreases.

C. Entropy of the metal box decreases; total entropy is unchanged.

D. Entropy of the metal box decreases; total entropy increases.

E. none of the above

Entropy and the second law

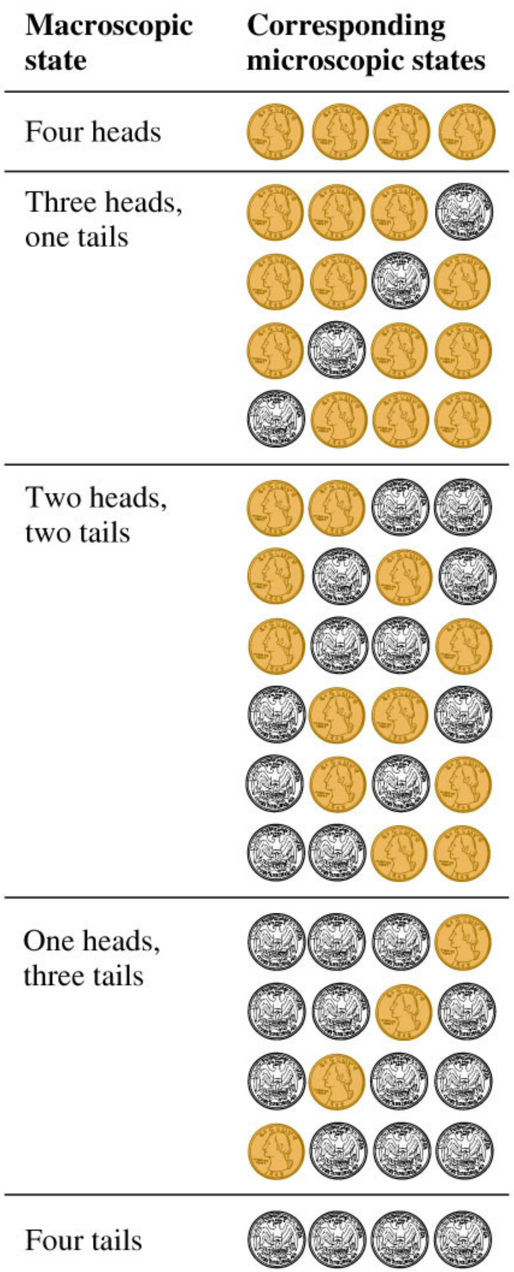
- The second law of thermodynamics can be stated in terms of entropy:

✓**No process is possible in which the total entropy decreases, when all systems taking part in the process are included.**

- The entropy of the ink–water system *increases* as the ink mixes with the water.

Microscopic interpretation of entropy

- Suppose you toss *N* identical coins on the floor.
- The most probable outcome of tossing *N* coins is that half are heads and half are tails.
- The reason is that this macroscopic state has the greatest number of corresponding microscopic states.



Microscopic interpretation of entropy

- Let w represent the number of possible microscopic states for a given macroscopic state.
- The entropy S of a macroscopic state can be shown to be given by:

Expression for entropy in microscopic terms

$$S = k \ln w$$

Number of microscopic states for the given macroscopic state

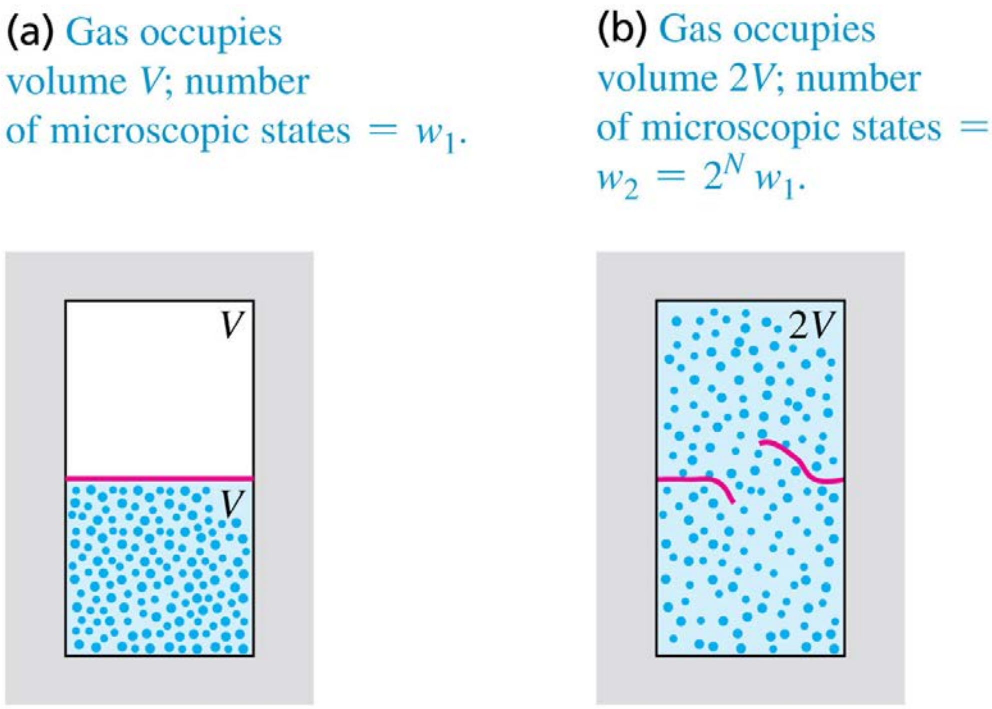
Boltzmann constant (gas constant per molecule)

- The difference in entropy between one state and another is,

$$\Delta S = S_2 - S_1 = k \ln w_2 - k \ln w_1 = k \ln \frac{w_2}{w_1}$$

A microscopic calculation of entropy change

- In a free expansion of N molecules in which the volume doubles, each molecule has twice as many possible sates after the partition is broken. Hence the number w2 of microscopic states when the gas occupies volume 2V is greater by a factor of 2^N.



$$\Delta S = k \ln \frac{w_2}{w_1} = k \ln 2^N = Nk \ln 2 = (nN_A)(R / N_A) \ln 2 = nR \ln 2$$