A model of a Stirling engine showing its simplicity. Unlike the steam engine or internal combustion engine, it has no valves or timing train. The heat source (not shown) would be placed under the brass cylinder

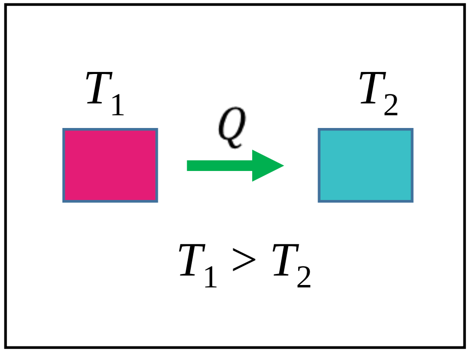
Chapter 16 The Second Law of Thermodynamics

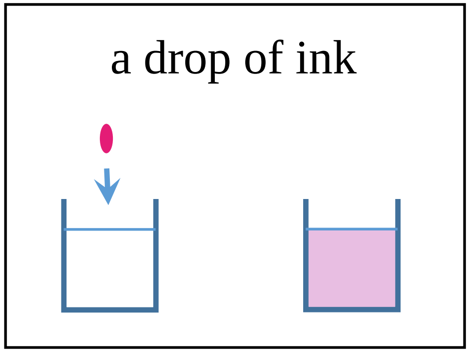
- To examine the directions of thermodynamic processes.
- To study heat engines.
- To understand internal combustion engines and refrigerators.
- To learn and apply the second law of thermodynamics
- To understand the Carnot engine: the most efficient heat engine.
- To learn the concept of entropy.

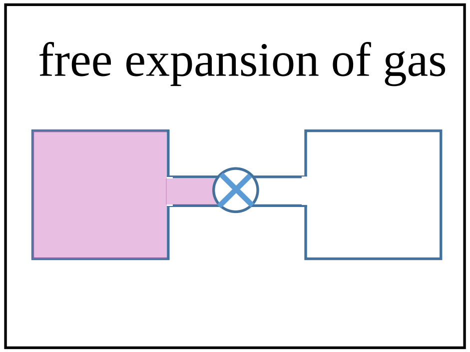
Stirling engine is a heat engine with cyclic compression and expansion producing mechanical work from heat energy

16.1 Directions of Thermodynamic Processes

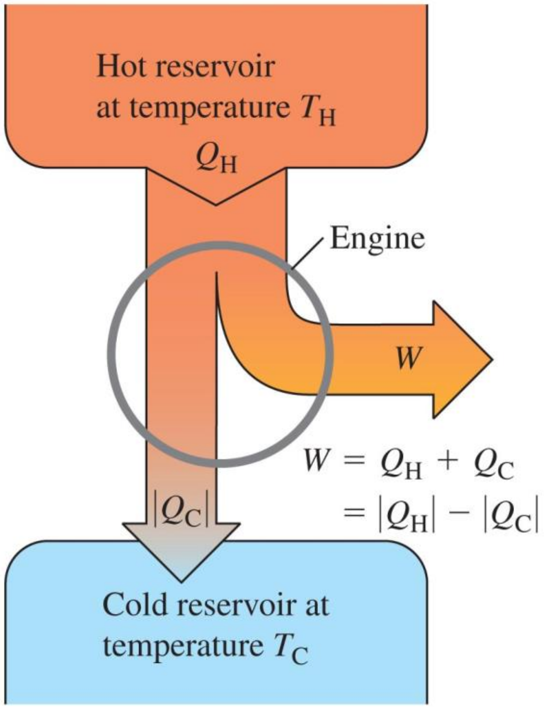
- Heat flows spontaneously from a "hot" object to a "cold" object.
- A process can be
  - Spontaneous
  - Non-spontaneous
  - Reversible
  - Irreversible
  - In equilibrium
- Overall, there can be an increase or decrease in order.
- Devices can interconvert order/disorder/energy.







16.2 Heat Engine



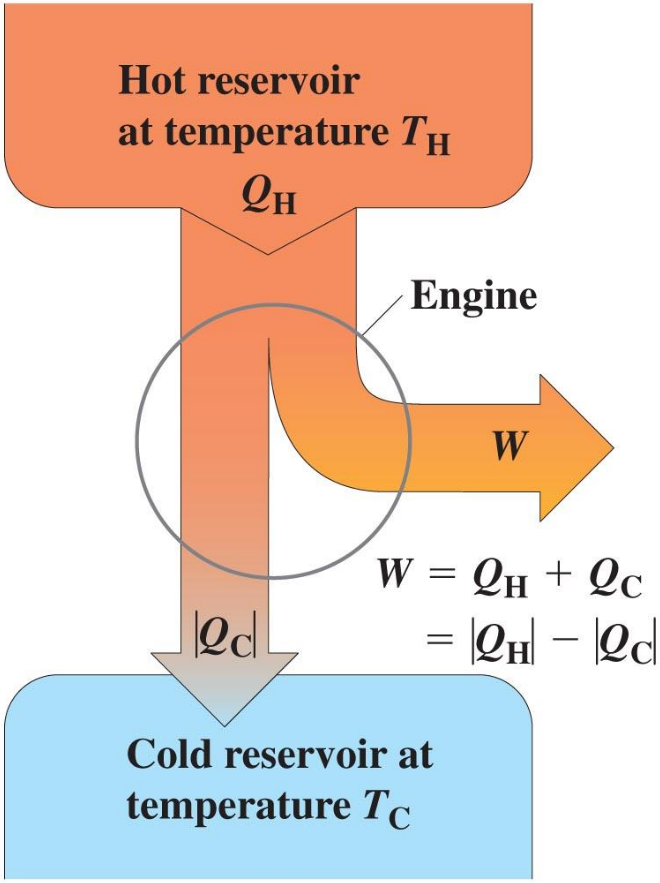
Energy flow diagram

- A heat engine works in cycles.
- A heat engine absorbs an amount of heat energy Q_H from the high-temperature reservoir.
- It does an amount of work W on the surrounding, and, it rejects an amount of heat energy Q_C to the low-temperature reservoir.
- After it complete a cycle, it returns to its initial state, or, $\Delta U = 0$.
- Apply the First Law of Thermodynamics, $Q - W = \Delta U = 0$. So, we have $W = Q = Q_H + Q_C = Q_H - |Q_C|$
- The thermal efficiency of a heat engine

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

Note: (a) Q_H is positive (absorbed into the "system").
(b) Q_C is negative (rejected from the "system").
(c) W is positive (done by the "system" on surrounding).

The second law of thermodynamics and heat engines



Why does heat always flow from hotter to colder places and not in reverse?

15.30

One-way processes are described by the second law of thermodynamics

it uses the concept of entropy = quantitative measure of the degree of disorder

heat engines, convert heat into work

refrigerators (transport heat from colder to hotter objects)

Heat engine:

cyclic process with

$\Delta U = Q - W = 0 \rightarrow Q = W$

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

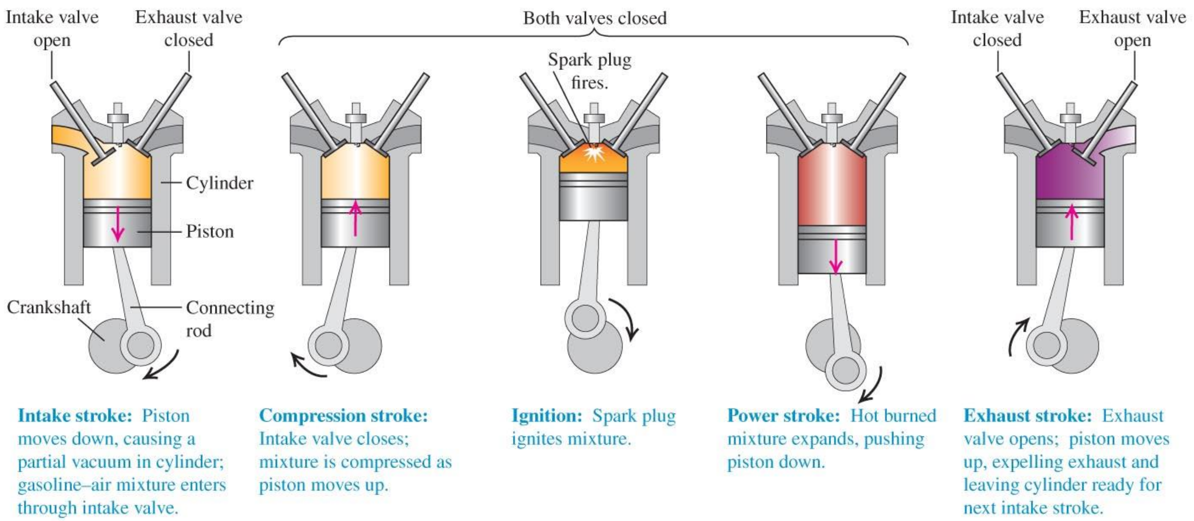
$W = Q =$ ideally $Q_H = W$ and $Q_C = 0$

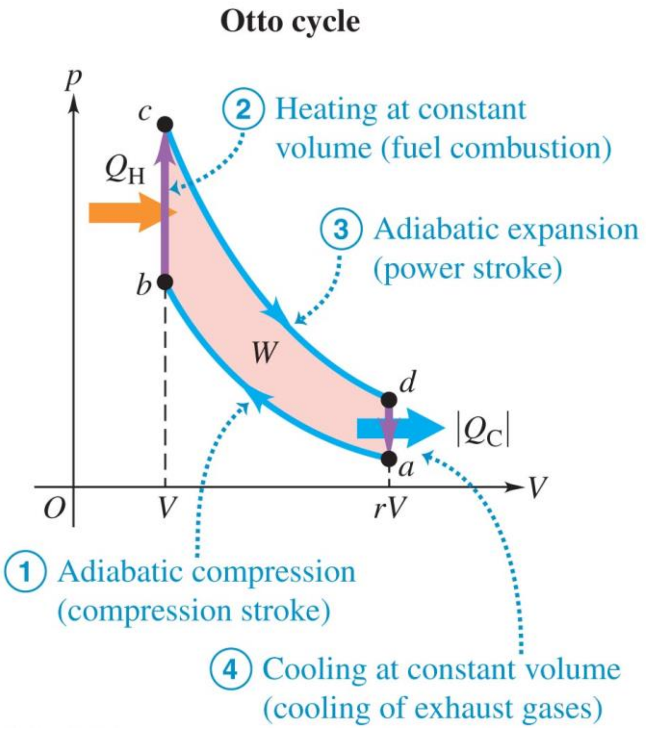
however in practice some heat is wasted

Thermal efficiency of a heat engine

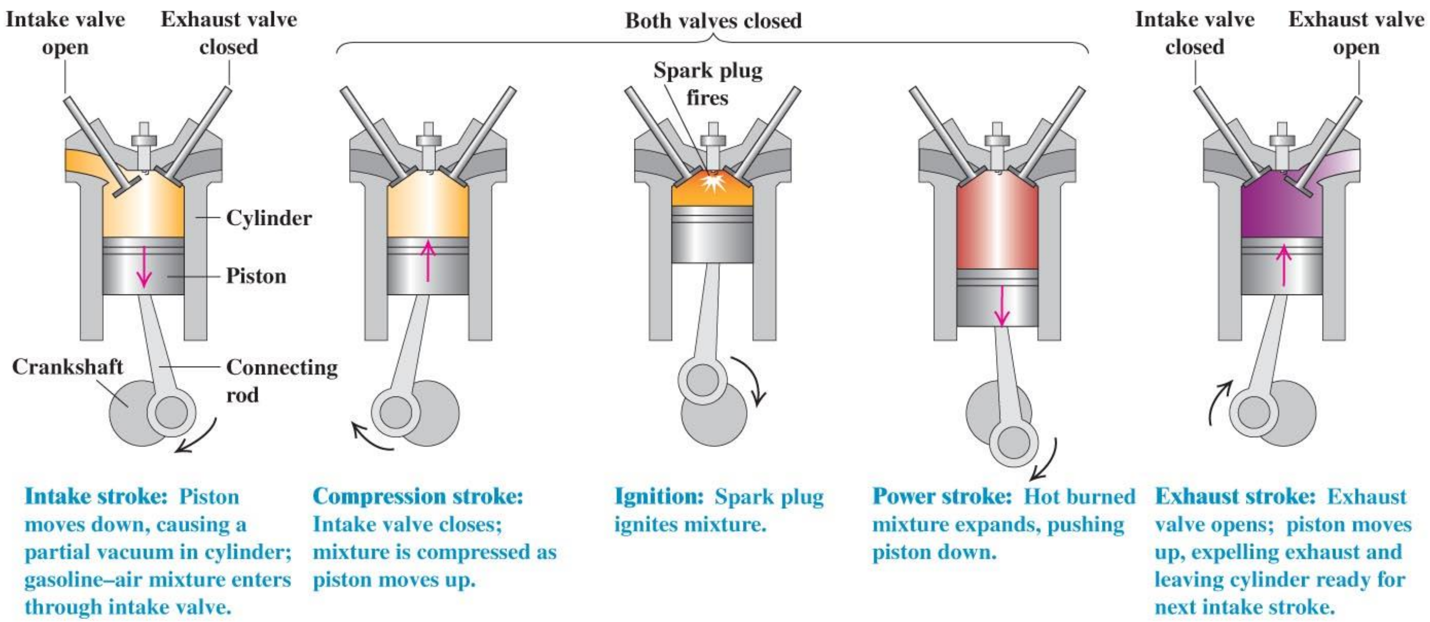
$e = \frac{W}{Q_H}$

16.3 Internal Combustion Engine





The ottocycle = gasoline engine

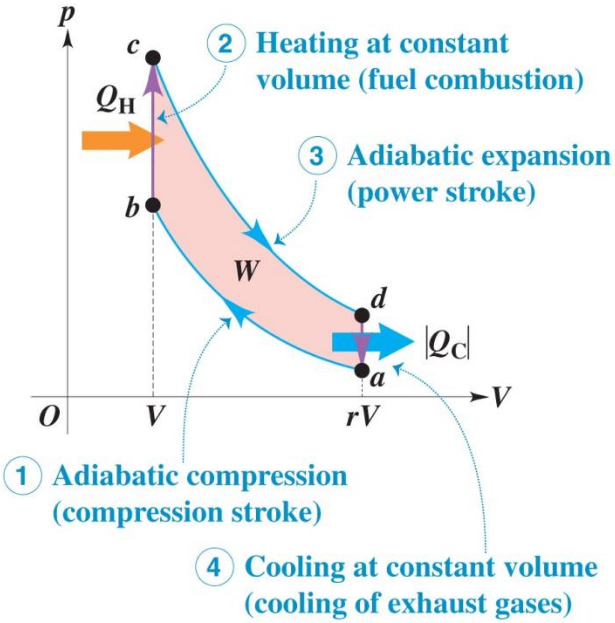


$$r = \text{compression ratio} = \frac{V_{max}}{V_{min}} = \frac{\text{piston down}}{\text{piston up}} \approx 8$$

3 types of heat engines:

1. Gasoline or otto engine e = 56%
2. Diesel engine e= 68%
3. Carnot engine most efficient heat engine e= 90% for large temp difference

Otto cycle



at a mixture enters
line a b
air-gasoline mixture is adiabatically compressed
at b ignition
line bc adiabatic expansi

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

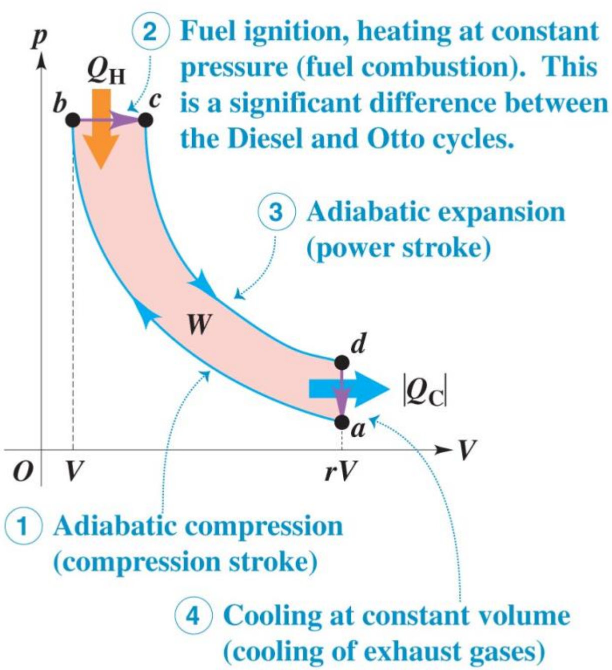
$$\gamma = \frac{C_p}{C_V}$$

e=0.56 r=8 otto

e=0.70 r=20 Diesel

Diesel cycle

For Diesel there is no fuel in the compression stroke and r can be large

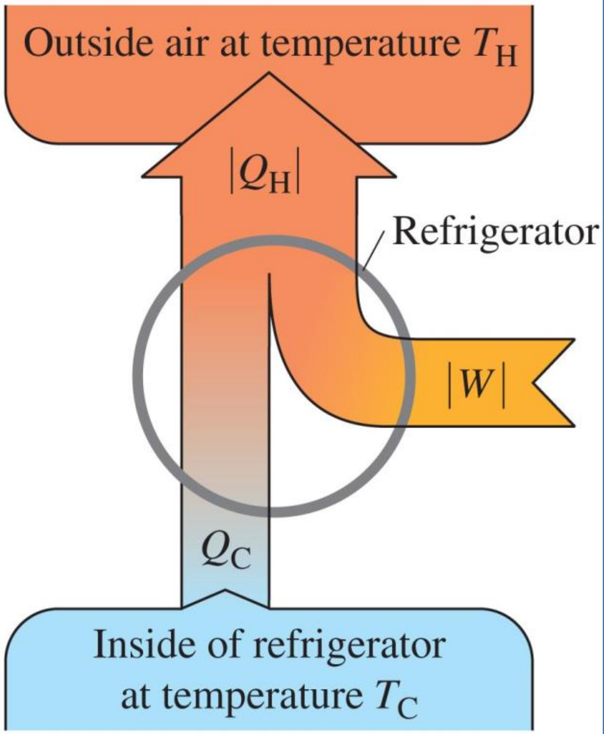


second law of thermodynamics

Experimental evidence suggests that it is not possible to build an engine that converts heat completely into work

No cyclic process can convert heat completely into work

16.4 Refrigerators---Heat Engine Running "Backward"



- A refrigerator also works in cycles.
- Work W is done on the refrigerator by a motor.
- The refrigerator absorbs an amount of heat Q_C from the low-temperature reservoir, and, it rejects an amount of heat Q_H to the high-temperature reservoir.
- It completes a cycle and returns to its initial state, $\Delta U = 0$.
- Apply the First Law of Thermodynamics, $Q - W = \Delta U = 0$,

  we have $\qquad W = Q = Q_c + Q_H = Q_C - |Q_H|$,

  or, $\qquad |Q_H| = Q_C - W = Q_C + |W|$
- The efficiency of a refrigerator

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

Note: (a) Q_H is negative (rejected from the "system").

(b) Q_C is position (absorbs into the "system").

(c) W is negative (done on the "system" by surrounding).

Refrigerators

$Q_c > 0$, $W < 0$ and $Q_H < 0$

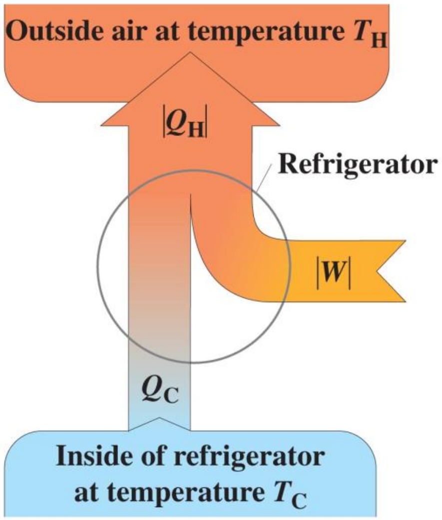
For a cyclic process $\Delta U = 0$

$$Q_H + Q_c - W = 0 \qquad Q_c - W = -Q_H$$

or because $|W| = -W$ and $|Q_H| = -Q_H$

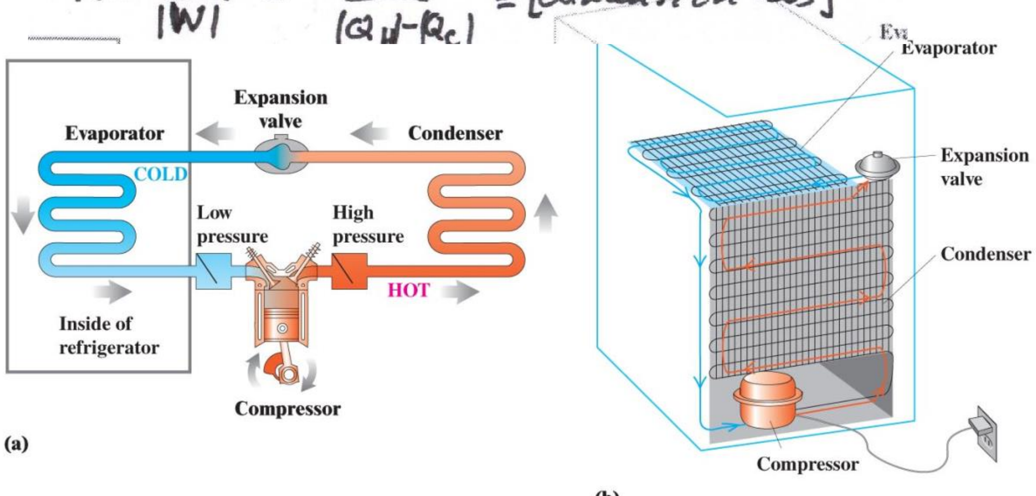
$$|Q_H| = |Q_c| + |W|$$

} heat leaving the working substance and given to the hot reservoir is always greater than the heat taken from the cold reservoir

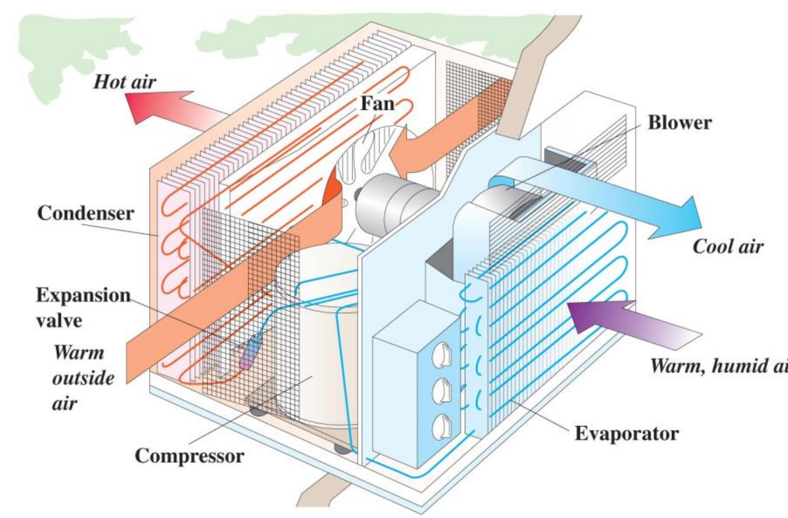


performance coefficient of a refrigerator

$$K = \frac{Q_c}{|W|} = \frac{|Q_c|}{|Q_H| - |Q_c|} = \text{[dimensionless]}$$



Refrigerator



Air conditioner

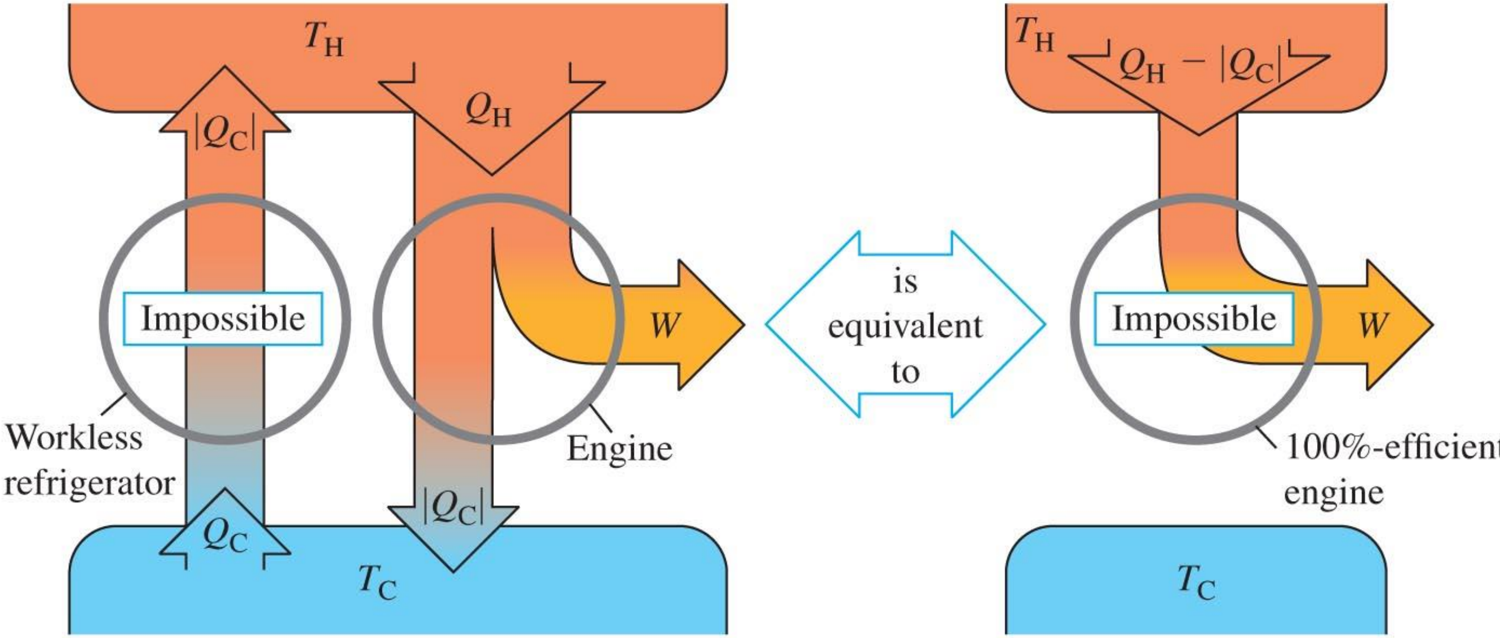
16.5 The Second Law of Thermodynamics

Equivalent Statements of the Second Law of Thermodynamics

● The Engine Statement
It is impossible for any heat engine to undergo a cyclic process in which it
absorbs heat from a reservoir at a single temperature and converts the heat
completely into mechanical work.

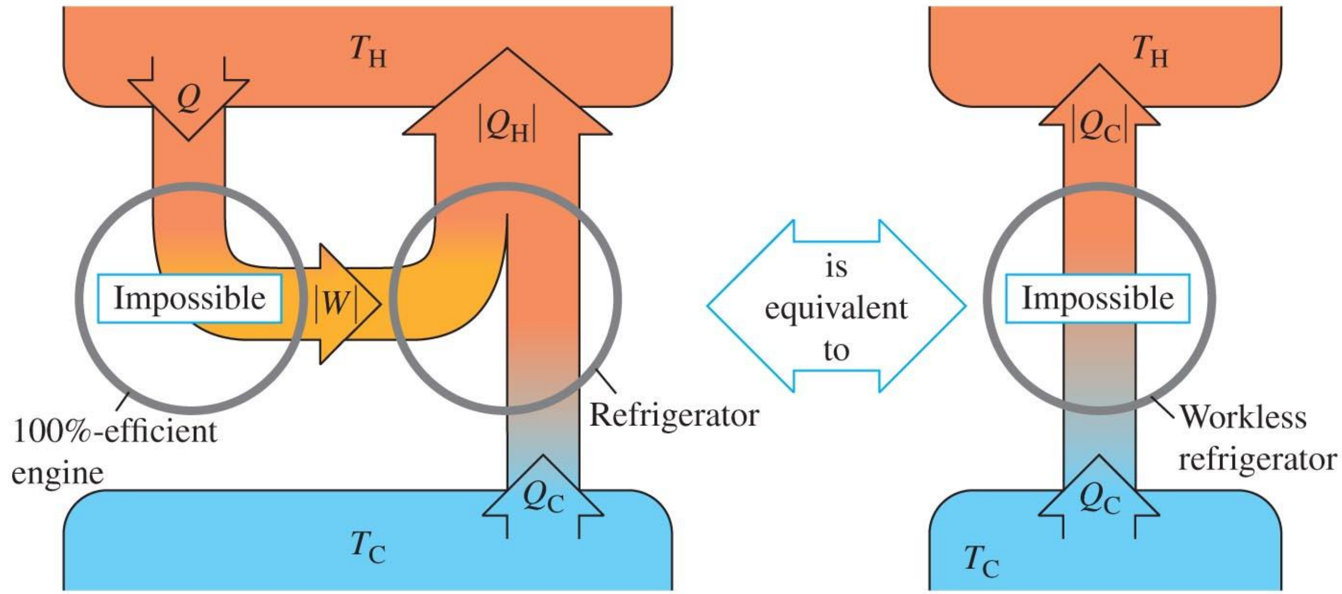
● The Refrigerator Statement
It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter object.

A "workless" refrigerator is impossible:
It would violate the "engine statement"



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.

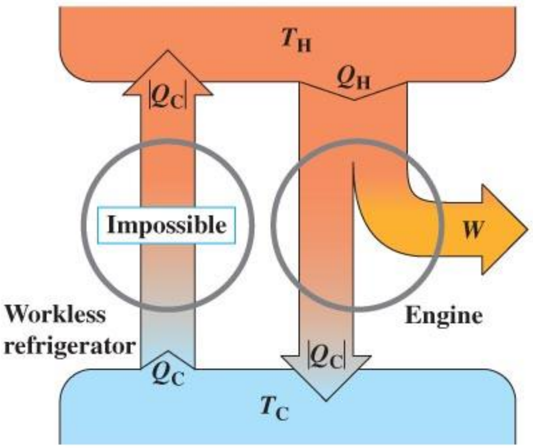
A “100% efficient” engine is impossible:
It would violate the “refrigerator statement”



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.

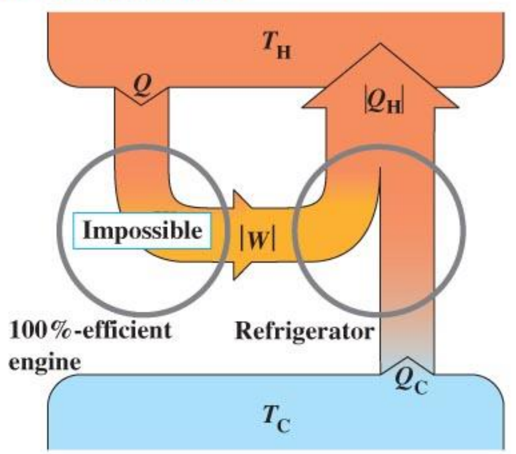
Second law of thermodynamics

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.



(a) The "engine" statement of the second law

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 net input of work.



(b) The "refrigerator" statement of the second law

Experimental evidence suggest that it is impossible to build a heat engine that converts heat completely into work (with efficiency of 100%)

<u>engine statement:</u>

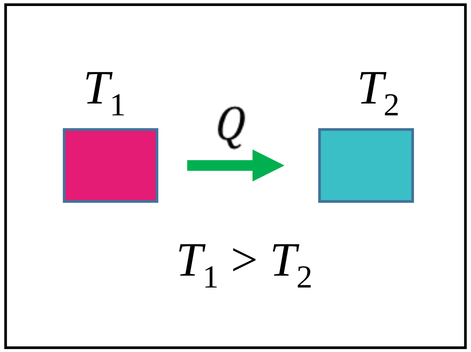
It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work with the system ending in the same state in which it began

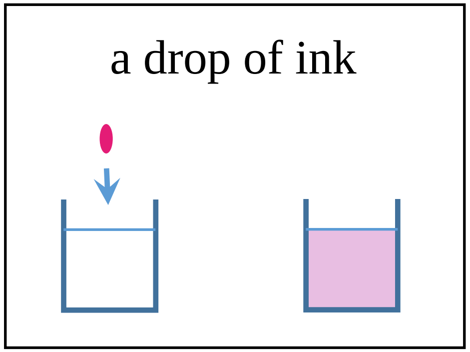
<u>refrigerator statement:</u>

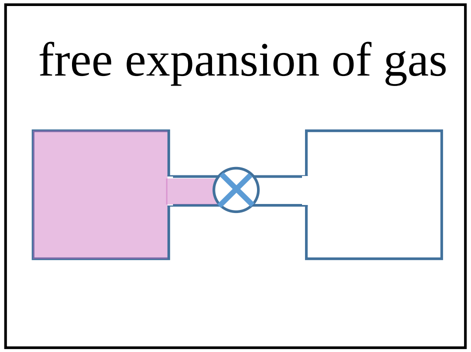
It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter object

The Essence of the Second Law of Thermodynamics

The one-way aspect of the processes occur in nature----irreversibility.







Machines of Perpetual Motion that Violate the Laws of Thermodynamics

- Perpetual Motion of the First Type

  Is it possible to build a machine, which, once started its motion, could repeat its motion all by itself and carry out work perpetually? No, it is not possible.

  This machine violates the First Law of Thermodynamics, which dictates that, in cyclic motion with $\Delta U = 0$,

$$W = Q$$

- Perpetual Motion of the Second Type

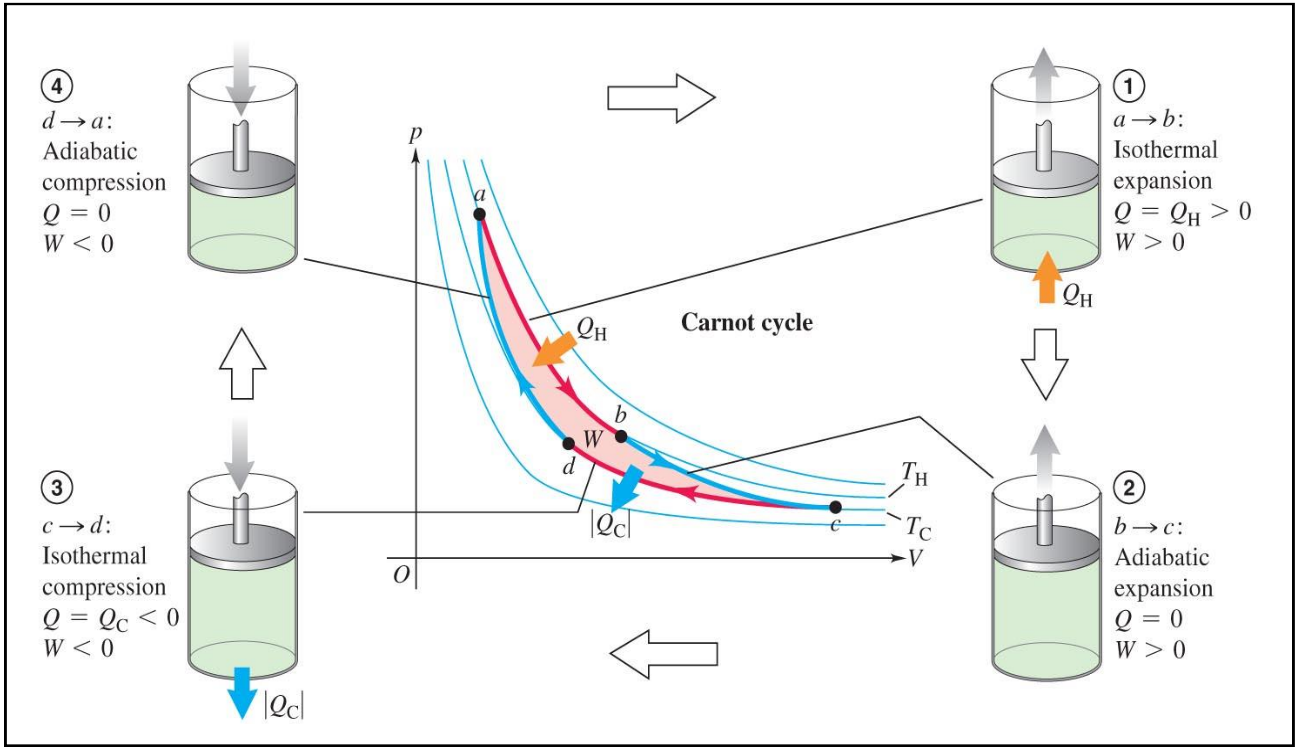
  Then, is it possible to build a machine that can take heat energy from a source and turn it 100% into work? No, it is not possible.

  This machine violates the Second Law of Thermodynamics, which dictates that part of the heat energy taken from a heat source must be rejected to a lower-temperature source,

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

16.6 The Carnot Engine---The Most Efficient Engine

- The Carnot Cycle is an ideal model of the heat engine.



If all the four processes are reversible, the efficiency is the highest possible.

It can be shown that

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

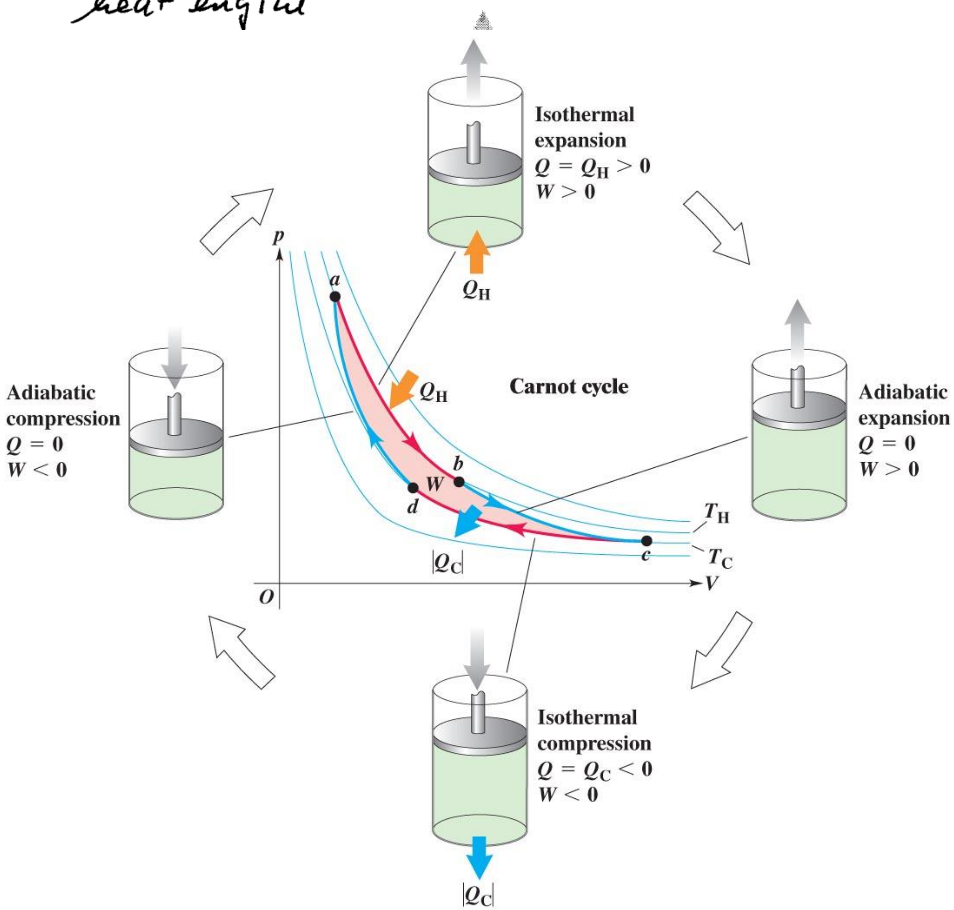
therefore, the efficiency

$$e = \frac{W}{Q_H} = \frac{Q_H + Q_C}{Q_H}$$

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

Try to avoid irreversible processes

Carnot engine = most efficient heat engine



Engine of maximum efficiency consistent with the second law of thermodynamics

$$e = 1 + \frac{Q_C}{Q_H}$$

for Carnot cycle engine

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

$$e = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}$$

Efficiency is the larger the larger the temperature difference

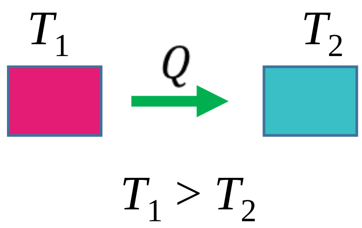
The gas expands isothermally at temperature T_H absorbing heat Q_H

It Expands adiabatically until its temperature drops to T_C

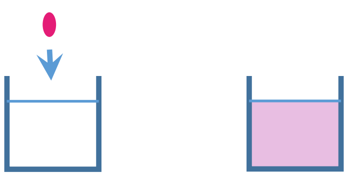
It is compressed isothermally at T_C rejecting heat Q_C

It is compressed adiabatically back to its initial state at temperature T_H

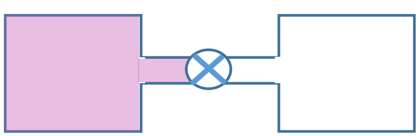
16.7 Entropy----Provides a quantitative measure of disorder



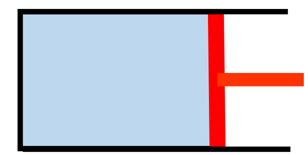
a drop of ink



free expansion of gas



Consider an infinitesimal isothermal expansion of an ideal gas:



$$\Delta U = 0,$$

$$Q = W = p\Delta V = \frac{nRT}{V}\Delta V$$

or,

$$\frac{Q}{T} = nR\frac{\Delta V}{V}$$

Since $\Delta V/V$ is a measure of disorder, the change in entropy is define as:

$$\Delta S = (S_2 - S_1) = \frac{Q}{T}$$

The Entropy Statement of the Second Law of Thermodynamics:

- It is impossible to have a process in which the total entropy decreases when all systems taking part in the process are included.
- It is impossible for the entropy of a closed system to decrease.

Entropy change in a reversible isothermal process with units: J/K

Problem 16.2-1

If a heat engine is 33 % efficient, how much work can you get by putting in 150 J of heat, and how much heat do you waste during each cycle?

$$e = \frac{W}{Q_H} \qquad W = Q_H + Q_C \qquad \left.\begin{matrix} W \\ Q_H \end{matrix}\right\} > 0 \qquad Q_C < 0$$

$$Q_H = 150 J$$

$$W = e Q_H = 0.33 \; 150 J = 50 J$$

$$Q_C = W - Q_H = 50 J - 150 J = -100 J$$ (wasted)

For an Otto engine with a compression ratio of 7.50, you have your choice of using an Ideal monatomic or ideal diatomic gas. Which one would give greater efficiency?

16.12. Set Up: $e = 1 - \frac{1}{r^{\gamma-1}}$. For a monatomic ideal gas $\gamma = 1.67$ and for a diatomic ideal gas $\gamma = 1.40$.

Solve: The monatomic gas gives a larger e. For a monatomic gas,

$$e = 1 - \frac{1}{7.50^{0.67}} = 0.741 = 74.1\%.$$

For a diatomic gas,

$$e = 1 - \frac{1}{7.50^{0.40}} = 0.553 = 55.3\%.$$

In one cycle a freezer uses 785 J of electrical energy in order to remove 1750 J of heat
From its freezer compartment at 10 F. a) what is the coefficient of performance
Of this freezer? b) how much heat does it expel into the room during this cycle?

16.14. Set Up: For a refrigerator, the coefficient of performance is $K = \frac{|Q_C|}{|W|}$. $|Q_C| = 1750\ \text{J}$ and $|W| = 785\ \text{J}$. $|Q_H| = |Q_C| + |W|$.

Solve: **(a)** $K = \frac{1750\ \text{J}}{785\ \text{J}} = 2.23$

(b) $|Q_H| = |Q_C| + |W| = 1750\ \text{J} + 785\ \text{J} = 2535\ \text{J}$

A refrigerator has a coefficient of performance of 2.10. Each cycle, it absorbs 3.4 E4 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-temp reservoir?

16.15. Set Up: For a refrigerator, $|Q_H| = |Q_C| + |W|$. $Q_C > 0$, $Q_H < 0$. $K = \dfrac{|Q_C|}{|W|}$.

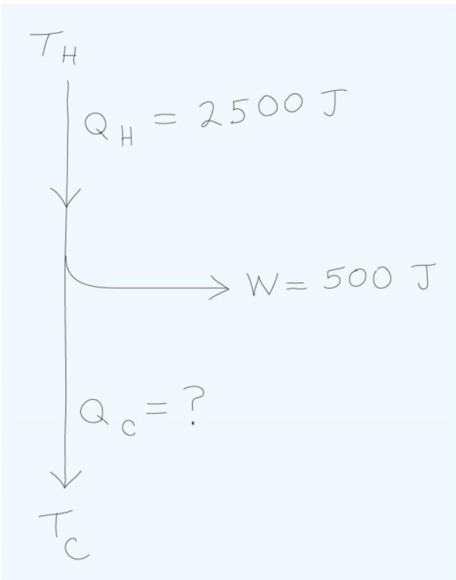
Solve: (a) $W = \dfrac{|Q_C|}{K} = \dfrac{3.40 \times 10^4\ \text{J}}{2.10} = 1.62 \times 10^4\ \text{J}$.

(b) $|Q_H| = 3.40 \times 10^4\ \text{J} + 1.62 \times 10^4\ \text{J} = 5.02 \times 10^4\ \text{J}$.

Reflect: More heat is discarded to the high temperature reservoir than is absorbed from the cold reservoir.

Example 16.1 Fuel consumption in a truck

The gasoline engine in a truck takes 2500 J of heat and delivers 500 J of mechanical work per cycle. Assume the heat of combustion $L_c = 5 \times 10^4$ J/g



(a) What is the thermal efficiency?

$$e = \frac{W}{Q_H} = \frac{500\,J}{2500\,J} = 0.2 = \boxed{20\%}$$

(b) How much heat is discarded in each cycle?

$$W = Q_H + Q_c$$
$$500\,J = 2500\,J + Q_c \qquad \boxed{Q_c = -2000\,J}$$

(c) How much gasoline is burnt in each cycle?

$$Q_H = m L_c \qquad m = \frac{Q_H}{L_c} = \frac{2500\,J}{5 \times 10^4\,J/g} = \boxed{0.05\,g}$$

(d) Assume the engine goes through 100 cycles/s, what is the power output in watts

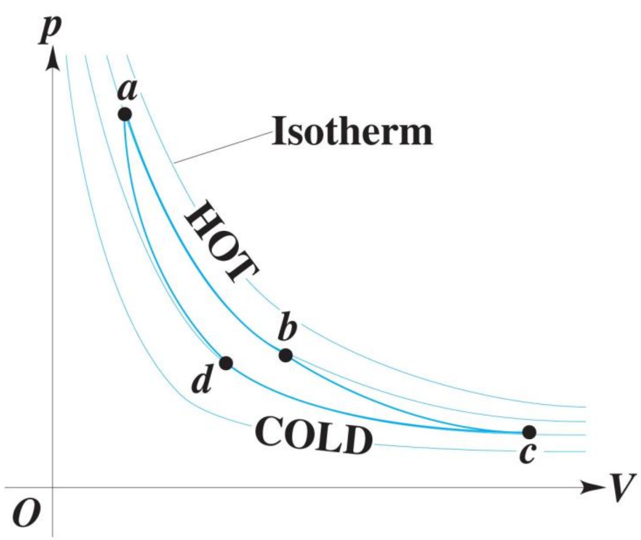
$$P = 500\,J/cycle \times 100\,cycles/s = 50000\,W = \boxed{50\,kW}$$

(e) How much gasoline is burnt per sec? per hour?

per sec: $0.05 \frac{g}{cycle}\, 100 \frac{cycles}{s} = \boxed{5\,g/s}$ per hour $5 \frac{g}{s} \frac{3600\,s}{h} = 18000\,g/h = \boxed{18\,kg/h}$

note: the density of gasoline $\rho = 0.7\,g/cm^3$ Volume $= 18000 \frac{g}{h} \frac{cm^3}{0.7\,g} = 25700\,cm^3 = 25.7\,l$

Problem 16.27 Carnot engine



Consider the pV diagram of the Carnot engine shown.

(a) If this engine is used as a heat engine what is the direction of the cycle, clockwise or counterclockwise?

<u>clockwise</u>, because for a heat engine W and Q_H are positive and Q_C is negative

More positive work is done during ab and bc than the magnitude of the negative work done in cd and da. The net work done in the cycle is positive and equal to the area enclosed by the loop

15. I A Carnot engine whose high-temperature reservoir is at 620 K takes in 550 J of heat at this temperature in each cycle and gives up 335 J to the low-temperature reservoir. (a) How much mechanical work does the engine perform during each cycle? (b) What is the temperature of the low-temperature reservoir? (c) What is the thermal efficiency of the cycle?

16.15. Set Up: $|Q_H| = |Q_C| + |W|$. $\dfrac{Q_C}{Q_H} = -\dfrac{T_C}{T_H}$. $Q_C < 0$, $Q_H > 0$. $e = \dfrac{W}{Q_H}$.

Solve: **(a)** $|W| = |Q_H| - |Q_C| = 550\text{ J} - 335\text{ J} = 215\text{ J}$.

(b) $\dfrac{T_C}{T_H} = -\dfrac{Q_C}{Q_H}$. $T_C = -T_H \dfrac{Q_C}{Q_H} = -(620\text{ K})\left(\dfrac{-335\text{ J}}{550\text{ J}}\right) = 378\text{ J}$.

(c) $e = \dfrac{W}{Q_H} = \dfrac{215\text{ J}}{550\text{ J}} = 0.391 = 39.1\%$

17. I A Carnot engine is operated between two heat reservoirs at temperatures of 520 K and 300 K. (a) If the engine receives 6.45 kJ of heat energy from the reservoir at 520 K in each cycle, how many joules per cycle does it reject to the reservoir at 300 K? (b) How much mechanical work is performed by the engine during each cycle? (c) What is the thermal efficiency of the engine?

16.17. Set Up: $|W| = |Q_H| - |Q_C|$. $\frac{Q_C}{Q_H} = -\frac{T_C}{T_H}$. $Q_C < 0$, $Q_H > 0$. $e = \frac{W}{Q_H}$.

Solve: (a) $Q_C = -Q_H\left(\frac{T_C}{T_H}\right) = -(6.45 \times 10^3\ \text{J})\left(\frac{300\ \text{K}}{520\ \text{K}}\right) = -3.72 \times 10^3\ \text{J}$

(b) $|W| = |Q_H| - |Q_C| = 6.45 \times 10^3\ \text{J} - 3.72 \times 10^3\ \text{J} = 2.73 \times 10^3\ \text{J}$

(c) $e = \frac{W}{Q_H} = \frac{2.73 \times 10^3\ \text{J}}{6.45 \times 10^3\ \text{J}} = 0.423 = 42.3\%$

16.9. Set Up: ca is at constant volume, ab has $Q = 0$, and bc is at constant pressure. For a constant pressure process $W = p\,\Delta V$ and $Q = nC_p\,\Delta T$. $pV = nRT$ gives $n\,\Delta T = \dfrac{p\,\Delta V}{R}$ so $Q = \left(\dfrac{C_p}{R}\right)p\,\Delta V$. If $\gamma = 1.40$ the gas is diatomic and $C_p = \frac{7}{2}R$. For a constant volume process $W = 0$ and $Q = nC_V\,\Delta T$. $pV = nRT$ gives $n\,\Delta T = \dfrac{V\,\Delta p}{R}$ so $Q = \left(\dfrac{C_V}{R}\right)V\,\Delta p$. For a diatomic ideal gas $C_V = \frac{5}{2}R$. 1 atm $= 1.013 \times 10^5$ Pa

(a) Find the pressure in pointa.

Solve: (a) $V_b = 9.0 \times 10^{-3}\ \text{m}^3$, $p_b = 1.5$ atm and $V_a = 2.0 \times 10^{-3}\ \text{m}^3$. For an adiabatic process $p_aV_a^\gamma = p_bV_b^\gamma$.

$$p_a = p_b\left(\frac{V_b}{V_a}\right)^\gamma = (1.5\ \text{atm})\left(\frac{9.0 \times 10^{-3}\ \text{m}^3}{2.0 \times 10^{-3}\ \text{m}^3}\right)^{1.4} = 12.3\ \text{atm}$$

(b) How much heat enters this gas per cycle?

(b) Heat enters the gas in process ca, since T increases.

$$Q = \left(\frac{C_V}{R}\right)V\,\Delta p = (\tfrac{5}{2})(2.0 \times 10^{-3}\ \text{m}^3)(12.3\ \text{atm} - 1.5\ \text{atm})(1.013 \times 10^5\ \text{Pa/atm}) = 5470\ \text{J}$$

$Q_H = 5470$ J

(c) How much heat leaves this gas per cycle?

(c) Heat leaves the gas in process bc, since T decreases.

$$Q = \left(\frac{C_p}{R}\right)p\,\Delta V = (\tfrac{7}{2})(1.5\ \text{atm})(1.013 \times 10^5\ \text{Pa/atm})(-7.0 \times 10^{-3}\ \text{m}^3) = -3723\ \text{J}$$

$Q_C = -3723$ J

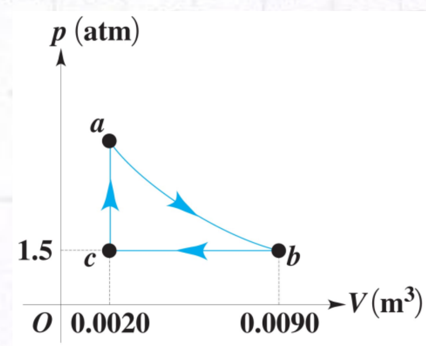
d. How much work does this engine do per cycle?

(d) $W = Q_H + Q_C = +5470\ \text{J} + (-3723\ \text{J}) = 1747\ \text{J}$

e. what is the thermal efficiency?

(e) $e = \dfrac{W}{Q_H} = \dfrac{1747\ \text{J}}{5470\ \text{J}} = 0.319 = 31.9\%$

Reflect: We did not use the number of moles of the gas.



consider the pV diagram of the heat engine that uses 0.25 mol of an ideal gas with γ = 1.4. The curved path ab is adiabatic.

Entropy and Disorder

Entropy provides a quantitative measure of disorder

consider an infinitesimal isothermal expansion of an ideal gas, in that process we add heat Q such that the temperature remains constant. To all Q is converted to W

$$Q = W = p\Delta V = \frac{nRT}{V}\Delta V \rightarrow \boxed{\frac{Q}{T} = nR\frac{\Delta V}{V}}$$

The gas is in a more disordered state after the expansion since the molecules move in a larger volume and have more randomness in position

special most simple case

In a reversible isothermal process the entropy change ΔS

$$\Delta S = S_2 - S_1 = \frac{Q}{T} \qquad \text{unit } \left[\frac{J}{K}\right]$$

Example 16.4 Entropy change in melting ice

Compute the change in entropy of 1 kg ice at 0°C when it is melted and converted to water at 0°C

$T = const = 273\ K$

$$Q = m L_f = 1\,kg \cdot 3.34 \times 10^5 \frac{J}{kg} = 3.34 \times 10^5\ J$$

$$\Delta S = \frac{Q}{T} = \frac{3.34 \times 10^3}{273} = \boxed{1220\ J/K}$$