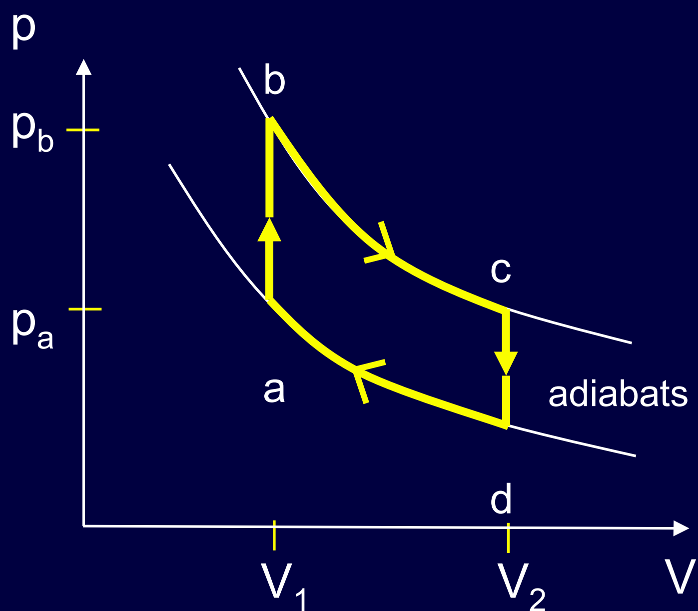
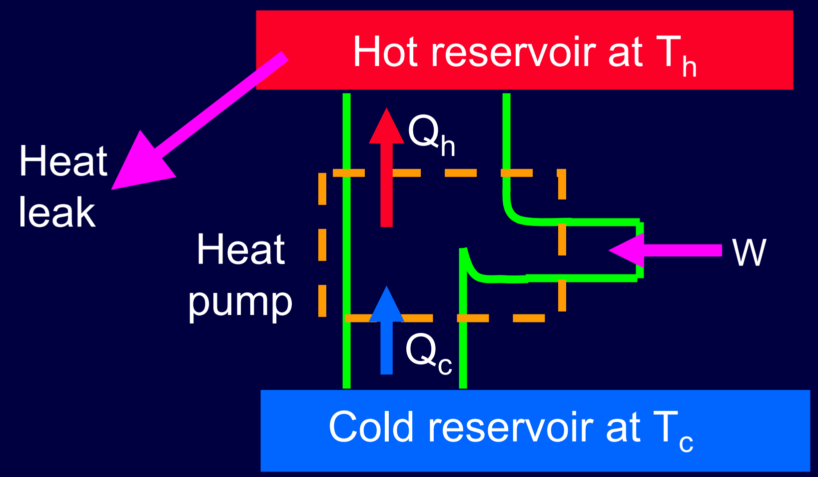
Lecture 15

Heat Engines

Review & Examples



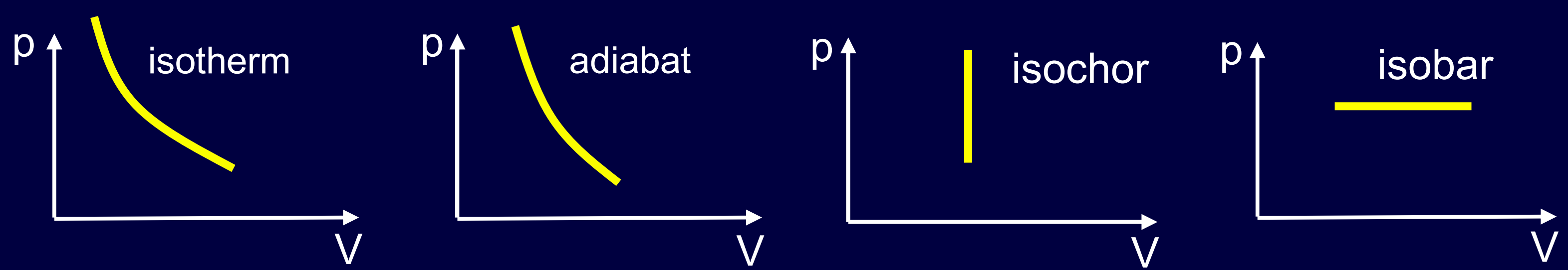


Irreversible Processes

Entropy-increasing processes are irreversible,
because the reverse processes would reduce entropy.
Examples:

- Free-expansion (actually, any particle flow between regions of different density)
- Heat flow between two systems with different temperatures.

Consider the four processes of interest here:
Isothermal: Heat flow but no T difference. Reversible
Adiabatic: Q = 0. No heat flow at all. Reversible
Isochoric & Isobaric: Heat flow between different T's. Irreversible
(Assuming that there are only two reservoirs.)



reversible reversible irreversible irreversible

ACT 1

1) The entropy of a gas increases during a quasi-static isothermal expansion.
What happens to the entropy of the environment?

a) $\Delta S_{env} < 0$ b) $\Delta S_{env} = 0$ c) $\Delta S_{env} > 0$

2) Consider instead the 'free' expansion (*i.e.*, not quasi-static) of a gas.
What happens to the total entropy during this process?

a) $\Delta S_{tot} < 0$ b) $\Delta S_{tot} = 0$ c) $\Delta S_{tot} > 0$

Remove the barrier

Solution

1) The entropy of a gas increases during a quasi-static isothermal expansion.
What happens to the entropy of the environment?

$\boxed{\text{a) } \Delta S_{env} < 0}$ b) $\Delta S_{env} = 0$ c) $\Delta S_{env} > 0$

Energy (heat) leaves the environment, so its entropy decreases.
In fact, since the environment and gas have the same T,
the two entropy changes cancel: $\Delta S_{tot} = 0$. This is a reversible process.

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What happens to the total entropy during this process?

a) $\Delta S_{tot} < 0$ b) $\Delta S_{tot} = 0$ $\boxed{\text{c) } \Delta S_{tot} > 0}$

There is no work or heat flow, so U_{gas} is constant. $\Rightarrow$ T is constant.
However, because the volume increases, so does the number of available states,
and therefore S_{gas} increases. Nothing is happening to the environment.
Therefore $\Delta S_{tot} > 0$. This is not a reversible process.

Review

Entropy in Macroscopic Systems

Traditional thermodynamic entropy: $S = k \ln\Omega = k\sigma$

We want to calculate S from macrostate information (p, V, T, U, N, *etc*.)
Start with the definition of temperature in terms of entropy:

$$\boxed{\frac{1}{kT} \equiv \left(\frac{\partial\sigma}{\partial U}\right)_{V,N}, \text{ or } \frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{V,N}}$$

The entropy changes when T changes: (We're keeping V and N fixed.)

$$dS = \frac{dU}{T} = \frac{C_V dT}{T} \Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T}$$

If C_V is constant: $$= C_V \int_{T_1}^{T_2} \frac{dT}{T} = C_V \ln\left(\frac{T_2}{T_1}\right)$$

ACT 2

Two blocks, each with heat capacity* $C = 1$ J/K are initially at different temperatures, $T_1 = 250$ K, $T_2 = 350$ K. They are then placed into contact, and eventually reach a final temperature of 300 K. (Why?) What can you say about the total change in entropy ΔS_{tot}?

a) $\Delta S_{tot} < 0$ b) $\Delta S_{tot} = 0$ c) $\Delta S_{tot} > 0$

$\boxed{T_1}$ $\boxed{T_2}$

$T_1 = 250$K

$T_2 = 350$K

$\boxed{T_f}\boxed{T_f}$

$T_f = 300$ K

Two masses each with heat capacity $C = 1$J/K*

*For a solid, $C = C_V = C_p$, to good approximation, since $\Delta V \approx 0$.**

Solution

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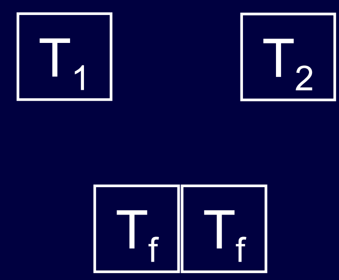

$T_1 = 250$K

$T_2 = 350$K

$T_f = 300$ K

Two masses each with heat capacity $C = 1$J/K*

a) $\Delta S_{tot} < 0$ b) $\Delta S_{tot} = 0$ c) $\boxed{\Delta S_{tot} > 0}$

This is an irreversible process, so there must be a net increase in entropy. Let's calculate ΔS:

$$\begin{aligned}\Delta S_{tot} &= C\ln\left(\frac{T_f}{T_1}\right) + C\ln\left(\frac{T_f}{T_2}\right) \\ &= C\ln\left(\frac{300}{250}\right) + C\ln\left(\frac{300}{350}\right) \\ &= C\ln\left(\frac{300^2}{250\times 350}\right) = (0.028)C = 0.028 \text{ J/K}\end{aligned}$$

The positive term is slightly bigger than the negative term.

*For a solid, $C = C_V = C_p$, to good approximation, because $\Delta V \approx 0$.

Example Process

To analyze heat engines, we need to be able to calculate ΔU, ΔT, W, Q, *etc*. for the processes that they use.

How much heat is absorbed by 3 moles of helium when it expands from V_i = 10 liters to V_f = 20 liters and the temperature is kept at a constant 350 K?
What are the initial and final pressures?

Solution

To analyze heat engines, we need to be able to calculate ΔU, ΔT, W, Q, *etc.* for the processes that they use.

How much heat is absorbed by 3 moles of helium when it expands from V_i = 10 liters to V_f = 20 liters and the temperature is kept at a constant 350 K?
What are the initial and final pressures?

$Q = W_{by}$	The 1st law. For an ideal gas, $\Delta T = 0 \rightarrow \Delta U = 0$. Positive Q means heat flows into the gas.
$W_{by} = nRT \ln(V_f/V_i) = 6048$ J	An expanding gas does work.
$p_i = nRT/V_i = 8.72\times10^5$ Pa $p_f = p_i/2 = 4.36\times10^5$ Pa	Use the ideal gas law, $pV = nRT$

Where is the heat coming from?
In order to keep the gas at a constant temperature, it must be put in contact with a large object (a "heat reservoir") having that temperature. The reservoir supplies heat to the gas (or absorbs heat, if necessary) in order to keep the gas temperature constant.
Very often, we will not show the reservoir in the diagram. However, whenever we talk about a system being kept at a specific temperature, a reservoir is implied.

Example Process (2)

Suppose a mole of a diatomic gas, such as O_2, is compressed adiabatically so the final volume is half the initial volume. The starting state is V_i = 1 liter, T_i = 300 K. What are the final temperature and pressure?

Solution

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$$p_i V_i^\gamma = p_f V_f^\gamma$$

Equation relating p and V for adiabatic process in α-ideal gas

$$\gamma = \frac{7/2}{5/2} = 1.4$$

γ is the ratio of C_p/C_V for our diatomic gas (=$(\alpha+1)/\alpha$).

$$p_f = p_i \left(\frac{V_i}{V_f}\right)^\gamma$$

Solve for p_f.

$$= \frac{nRT_i}{V_i}\left(\frac{V_i}{V_f}\right)^\gamma$$

We need to express it in terms of things we know.

$$= 6.57 x 10^6 \text{ Pa}$$

$$T_f = \frac{p_f V_f}{nR} = 395 \text{ K}$$

Use the ideal gas law to calculate the final temperature.

$$T_i^\alpha V_i = T_f^\alpha V_f$$

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{\frac{1}{\alpha}} = 395 \text{ K}$$

Alternative: Use the equation relating T and V for an adiabatic process to get the final temperature. α = 5/2

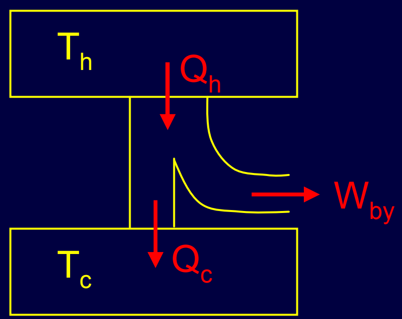
Helpful Hints in Dealing with Engines and Fridges

Sketch the process (see figures below).
Define Q_h and Q_c and W_{by} (or W_{on}) as positive and show directions of flow.

Determine which Q is given.

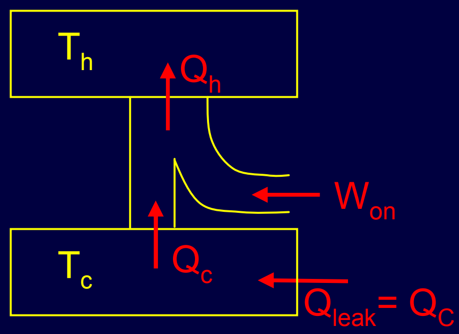
Write the First Law of Thermodynamics (FLT).

We considered three configurations of Carnot cycles:

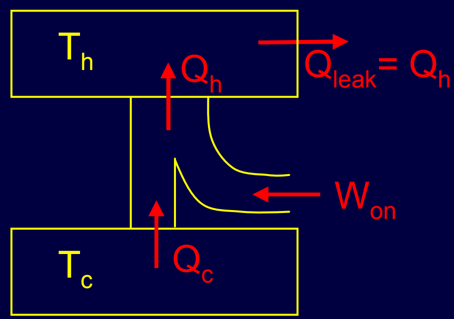


Engine:
We pay for Q_h,
we want W_{by}.
$W_{by} = Q_h - Q_c = \varepsilon Q_h$
Carnot: $\varepsilon = 1 - T_c/T_h$

This has large ε when $T_h - T_c$ is large.



Refrigerator:
We pay for W_{on},
we want Q_c.
$Q_c = Q_h - W_{on} = K W_{on}$
Carnot: $K = T_c/(T_h - T_c)$



Heat pump:
We pay for W_{on},
we want Q_h.
$Q_h = Q_c + W_{on} = K W_{on}$
Carnot: $K = T_h/(T_h - T_c)$

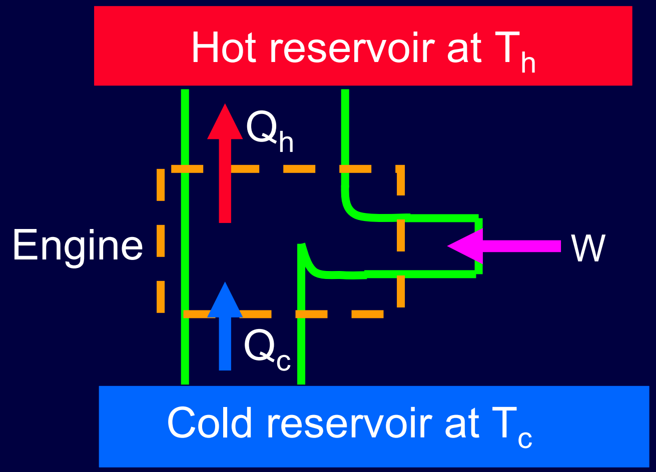
These both have large K when $T_h - T_c$ is small.

ACT 3:
Entropy Change in Heat Pump

Consider a Carnot heat pump.

1) What is the sign of the entropy change of the hot reservoir during one cycle?

a) $\Delta S_h < 0$ b) $\Delta S_h = 0$ c) $\Delta S_h > 0$



2) What is the sign of the entropy change of the cold reservoir?

a) $\Delta S_c < 0$ b) $\Delta S_c = 0$ c) $\Delta S_c > 0$

3) Compare the magnitudes of the two changes.

a) $|\Delta S_c| < |\Delta S_h|$ b) $|\Delta S_c| = |\Delta S_h|$ c) $|\Delta S_c| > |\Delta S_h|$

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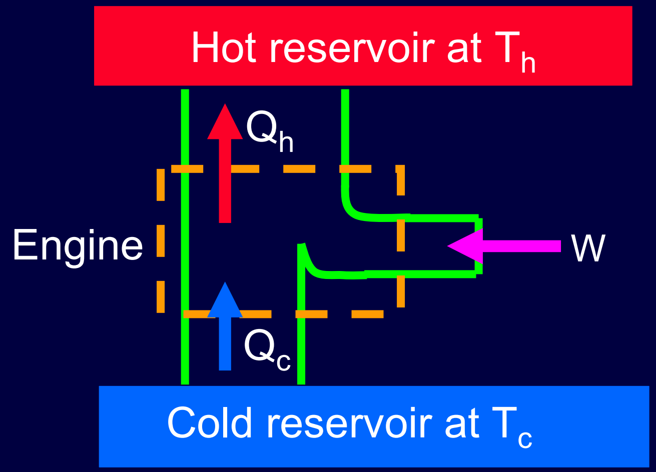
Energy (heat) is entering the hot reservoir, so the number of available microstates is increasing.



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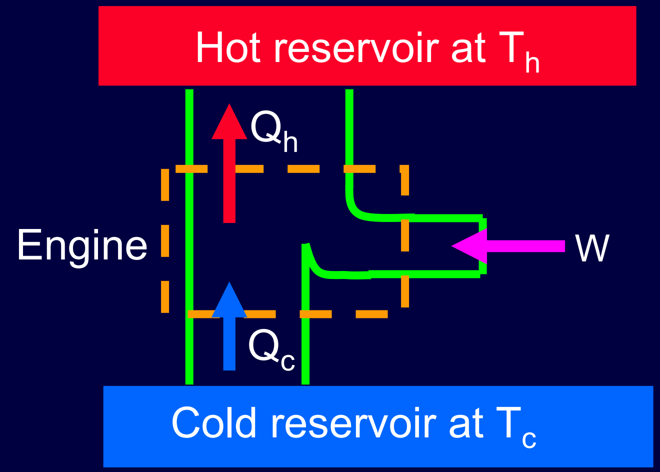

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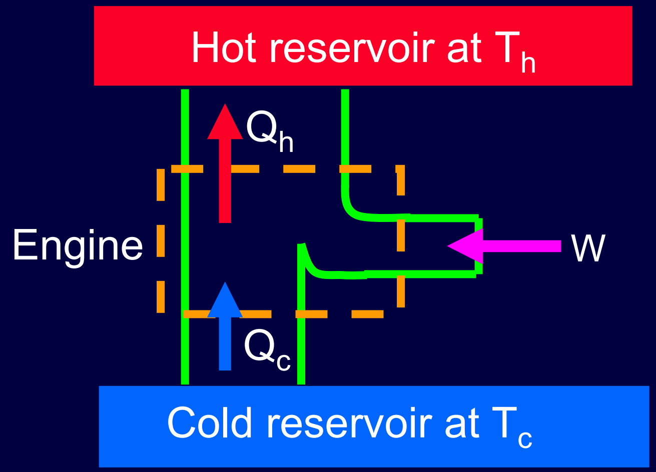

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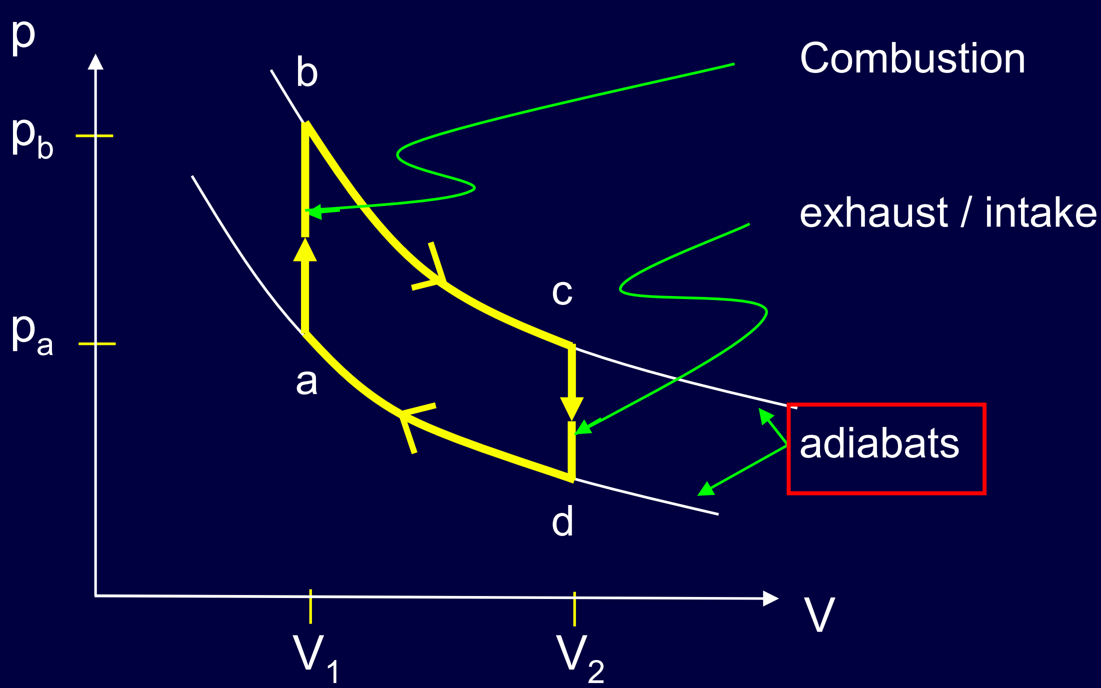
It's a reversible cycle, so $\Delta S_{tot} = 0$. Therefore, the two entropy changes must cancel. Remember that the entropy of the "engine" itself does not change.

Example: Gasoline Engine

It's not really a heat engine because the input energy is via fuel injected directly into the engine, not via heat flow. There is no obvious hot reservoir. However, one can still calculate work and energy input for particular gas types.

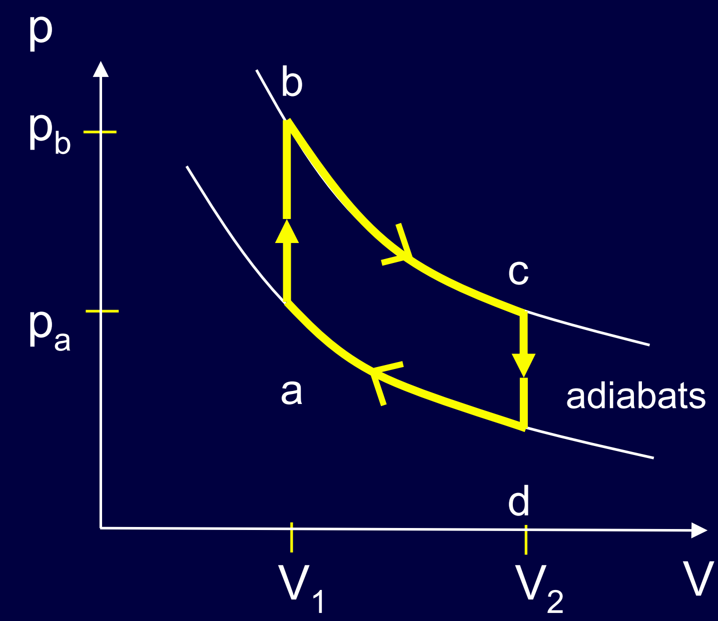
We can treat the gasoline engine as an Otto cycle:



b→c and d→a are nearly adiabatic processes,
because the pistons move too quickly for much heat to flow.

Solution

Calculate the efficiency:



$$Q_{in} = C_v(T_b - T_a)$$

$$W_{by} = W_{b\to c} - W_{d\to a}$$

$$W_{b\to c} = U_b - U_c = C_v(T_b - T_c) \quad \text{because } Q_{b\to c} = 0$$

$$W_{d\to a} = U_d - U_a = C_v(T_d - T_a) \quad \text{because } Q_{d\to a} = 0$$

$$W_{by} = C_v(T_b - T_c) - C_v(T_a - T_d)$$

$$\varepsilon = \frac{W_{by}}{Q_{in}} = \frac{C_v(T_b - T_c) - C_v(T_a - T_d)}{C_v(T_b - T_a)} = 1 - \frac{(T_c - T_d)}{(T_b - T_a)}$$

Solution

Write it in terms of volume instead of temperature.
We know the volume of the cylinders.

$$\varepsilon = 1 - \frac{(T_c - T_d)}{(T_b - T_a)}$$

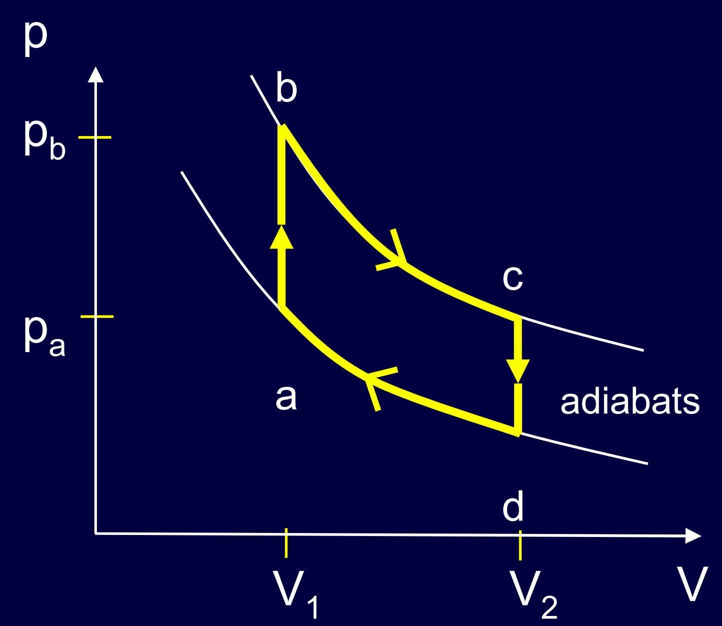
$$T_c^{\alpha} V_2 = T_b^{\alpha} V_1 \Rightarrow T_c = T_b (V_1 / V_2)^{1/\alpha}$$

$$T_d^{\alpha} V_2 = T_a^{\alpha} V_1 \Rightarrow T_d = T_a (V_1 / V_2)^{1/\alpha}$$

$$\therefore \frac{(T_c - T_d)}{(T_b - T_a)} = \frac{(T_b - T_a)(V_1 / V_2)^{1/\alpha}}{(T_b - T_a)}$$

$$= \left(\frac{V_1}{V_2}\right)^{1/\alpha} = \left(\frac{V_2}{V_1}\right)^{-1/\alpha} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}$$

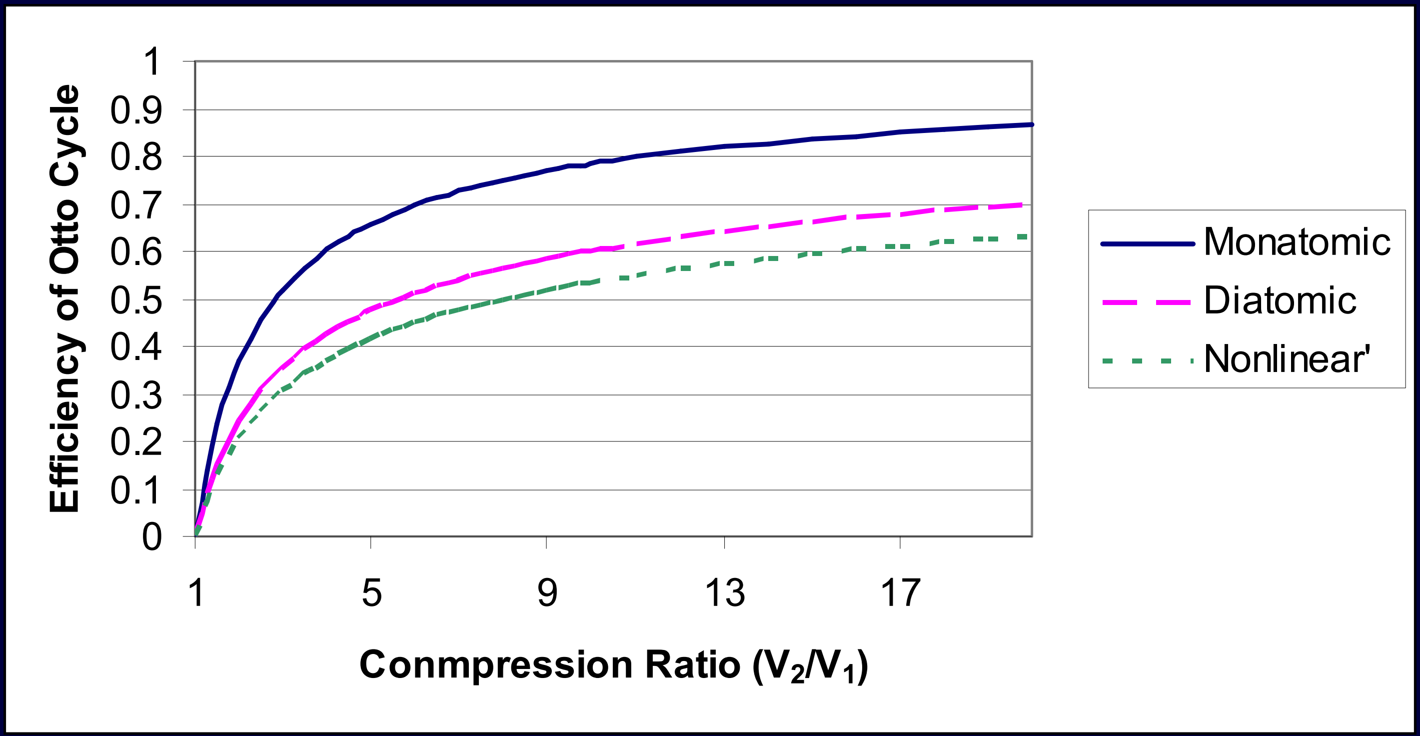
$$\varepsilon = 1 - \left(\frac{V_2}{V_1}\right)^{1-\gamma}$$



Compression ratio $\equiv V_2/V_1 \approx 10$
γ = 1.4 (diatomic gas) $\rightarrow \varepsilon$ = 60%

(in reality about 30%, due to friction etc.)

Solution



Why not simply use a higher compression ratio?

- If V_2 big, we need a huge, heavy engine (OK for fixed installations).
- If V_1 small, the temperature gets too high, causing premature ignition. High compression engines need high octane gas, which has a higher combustion temperature.

Free Energy Example

Suppose we have a liter of water at $T = 100°$ C.
What is its free energy, if the environment is $T = 20°$ C?
Verify the result by calculating the amount of work we could obtain.
Remember that $c_{H2O} = 4186$ J/kg·K.

Solution

Suppose we have a liter of water at T = 100° C.
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Remember that c_{H2O} = 4186 J/kg·K.

$\Delta F = \Delta U - T\Delta S$, where T is the temperature of the environment.
$\Delta U = mc\Delta T$ = 1 kg * 4186 J/kg·K * 80 K = 3.349×10^5 J.
$\Delta S = mc \ln(T_{H2O}/T_{env})$ = 1011 J/K
$\Delta F = 3.87\times10^4$ J

Remember to measure temperature in Kelvin.
Otherwise, you'll get the entropy wrong.

Solution

Suppose we have a liter of water at T = 100° C.
What is its free energy, if the environment is T = 20° C?
Verify the result by calculating the amount of work we could obtain.
Remember that c_{H2O} = 4186 J/kg·K.

If we run a Carnot engine, the efficiency at a given water temperature is:
E(T) = 1 - T/T_{env}. So, for each small decrease in water temperature, we get this much work out of the engine:

dW = εQ = -εmc dT
Thus, the total work obtained as T drops from 100° C to 20° C is:

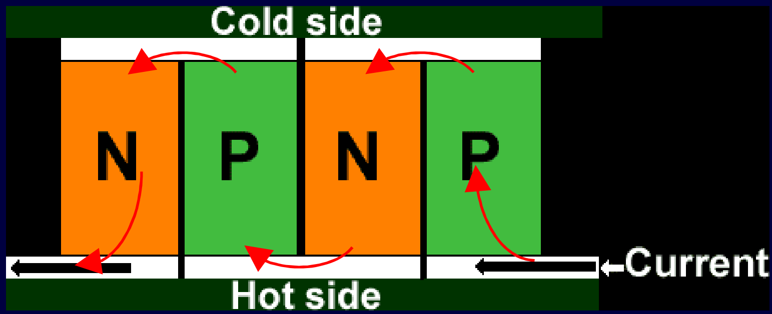
$$W = -mc\int_{373}^{293}\left(1-\frac{293}{T}\right)dT$$

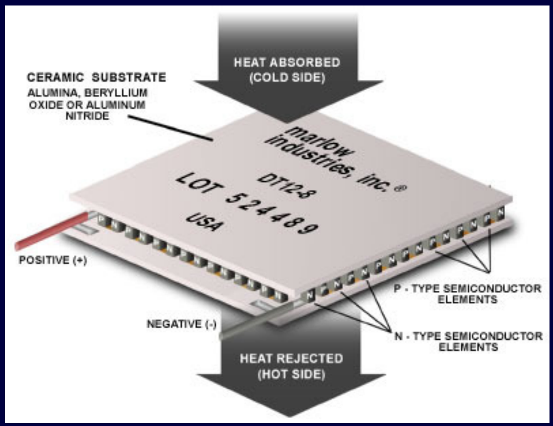
$$= \left(4186\text{ J/K}\right)\left[T-\left(293\text{ K}\right)\ln\left(\frac{373}{293}\right)\right]_{293}^{373}$$

$$= 3.87\times10^{4}\text{ K}$$

Non-mechanical Example: Peltier Cooler

Electrons in an n-type semiconductor have larger U than electrons in a p-type semiconductor. Therefore, if we push current through a series of n-p and p-n junctions, as shown, the electrons are cooled (because they slow down) at p-n and heated at n-p. This geometry gives us a hot and cold side.



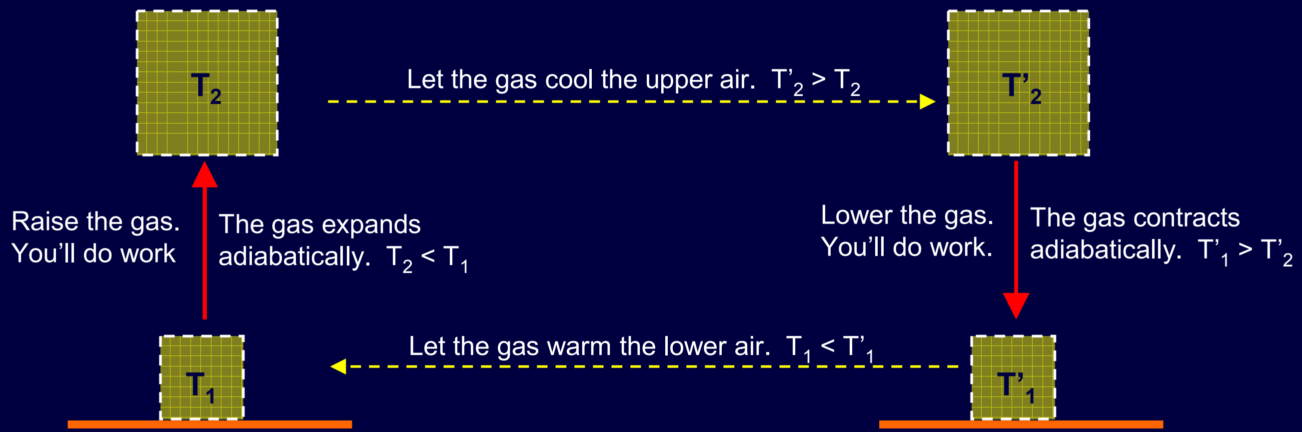


These devices aren't as efficient as conventional refrigerators, but are much more compact (and don't have mechanical parts). One can obtain tens of degrees of ΔT.

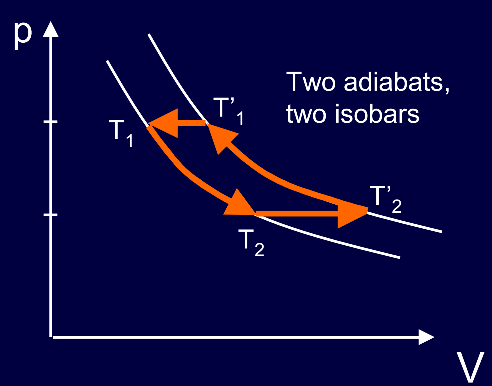
Despite the radically different construction, this heat pump obeys the same limits on efficiency as the gas-based pumps, because these limits are based on the 1st and 2nd laws, not on any details.

Peltier Cooler (2)

Here's the mechanical equivalent of a Peltier cooler. Raise and lower some gas (*i.e.*, between high and low potential). The raising and lowering is fast, so there is little heat flow, and the pressure at any height is the ambient air pressure (*i.e.*, it decreases with height).



Note: You must do work when raising **and** lowering the gas, due to the buoyancy (*i.e.*, the mgh energy), which is not described by the pV diagram.



This refrigerator does not achieve Carnot efficiency, because both of the processes represented by the horizontal arrows involve irreversible heat flow between objects at different temperatures.