Chapter 20

The Second Law of Thermodynamics

PowerPoint® Lectures for
University Physics, Twelfth Edition
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Topics for Chapter 20

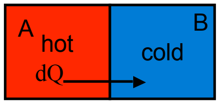
- I. Irreversible processes
- II. Definition of entropy and the Second Law
- III. Heat engine
- IV. Reversible heat engine, most efficient heat engine, the Carnot Cycle
- V. Refrigerator

I. Natural directions for thermodynamic processes

- Heat naturally flows from an hot object to a cold object ("naturally" means occurs spontaneously without the need of an external force)
- A piece of iron naturally gets rusty with time rather than gets shiny
- An orderly room naturally becomes disorder with time.
- These processes reflect nature's tendency to go from a non-equilibrium (a more ordered state) to an equilibrium state (a more disordered state) (According to statistical mechanics, the more disordered state is more probable, hence it tends to occur.)
- These processes are called ***"irreversible"*** process because their reverse processes (e.g. heat flow from cold object to hot object) do not occur naturally,.
- However, the reverse processes can occur by supplying energy to force order from disorder (e.g. a refrigerator moves heat from cold object to hot object, but you have to supply energy to the refrigerator).

II. Entropy and the Second Law of Thermodynamics

- The Second Law of Thermodynamics defines a state variable called "entropy" (S) to quantify the direction of natural processes. S is a function of (T,V,N), see example below

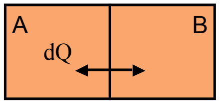


Non-equilibrium

$T_A^{\,i} > T_B^{\,i}$

The total initial entropy

$S_i = S_A(T_A^{\,i}) + S_B(T_B^{\,i})$



Equilibrium

$T_A^{\,f} = T_B^{\,f} = T^f$

The total final entropy

$S_f = (S_A(T^f) + S_B(T^f))$

Second Law : $S_f > S_i$ (the equilibrium state is more probable)

Calculate Entropy Change

Non-equilibrium — $T_A^i > T_B^i$

Equilibrium — $T_A^f = T_B^f$

If the process occurs "slowly", then the change in entropy is defined as:

$$dS \equiv \frac{dQ}{T} \Rightarrow dS_{total} = \frac{-dQ}{T_A} + \frac{Q}{T_B} > 0 \quad (\text{as long as } T_A > T_B; dS_{total} = 0 \ \text{when} T_A = T_B)$$

That is, the total entropy of system keep increasing by transferring heat from the hot object to the cold object, the entropy stops changing when the two objects are in thermal equilibrium (same temperature).

Note: $\frac{-Q}{T_A} < 0 \Rightarrow$ entropy of hot object decreases (heat is removed)

$\frac{Q}{T_B} > 0 \Rightarrow$ entropy of cold object increase (heat is heat). Combined entropy change is positive.

** Since T_A *and* T_B changes during the process, the overal change in entropy is given by an integral:

$$S_f - S_i \equiv \Delta S = \int_i^f \frac{-dQ}{T_A} + \frac{dQ}{T_B}$$

Second Law of Thermodynamics

If $\Delta S_{total} > 0$, then
the process is naturally occurring
and it is "irreversible".

If $\Delta S_{total} = 0$, then
the process is deemed "reversible".
Note: This is an idealized situation where the system is already at equilibrium, hence the process will proceed infinitestimally slow.

If $\Delta S_{total} < 0$, then
this process cannot occurred.

The Second Law of Thermodynamics is often stated as followed:
"In a closed system, the entropy can never decrease".

III. Use First Law and Second Law to analyse Heat engine

Heat Engine:
(1) Absorbs heat (Q_h) from a hot reservoir at T_h.
(2) Performs work (W).
(3) Expel remaining energy as heat (Q_c) to a cold reservoir at T_c.

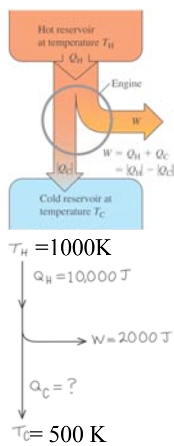
First Law: $Q_h = W + Q_c$

Efficiency of heat engine:

$$e \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

Second Law: $\Delta S \geq 0$ places a restriction on the maximum efficiency for a given set of T_h and T_c (see next slide).

* A temperature reservoir is a system with a very large heat capacity such that its temperature remains relatively the same when small amount of heat is added or removed from it, for example, a large tub of water or the ocean.



III. Use Second Law to determine max. efficiency of a heat engine

Refer to diagram on the right.

$$e = \frac{W}{Q_h} = \frac{8{,}000J}{10{,}000J} = 0.8$$

$Q_c = Q_h - W = 10{,}000J - 8{,}000J = 2{,}000J$

Is this engine possible?

Calculate ΔS_{total}.

$$\Delta S_{toal} = \Delta S_{\text{hot reservoir}} + \Delta S_{\text{cold reservoir}} + \Delta S_{\text{engine cycle}}$$

$$= -\frac{10{,}000J}{1{,}000K} + \frac{2{,}000J}{400K} + 0 < 0 \Rightarrow \text{ not possible!!}$$

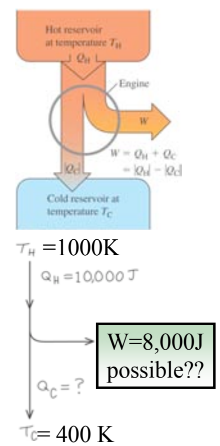
What is the minimum Qc without violating the second Law?

Minimum Q_c when $\Delta S_{total} = 0 \Rightarrow Q_c^{min.} = 4{,}000J$

(Q_c can be larger than $4{,}000J$, it is ok to have $\Delta S_{total} > 0$)

Minimum $Q_c \Rightarrow$ Maximum W = 10,000J - 4,000J = 6,000J

$$\Rightarrow \text{Max. e} = \frac{W^{max}}{Q_h} = \frac{6{,}000J}{10{,}000J} = 0.6$$



III. Use Second Law to determine max. efficiency of a heat engine

Recap and general formula:

What is the minimum Qc without violating the second Law?

Minimum Q_c when $\Delta S_{total} = 0$

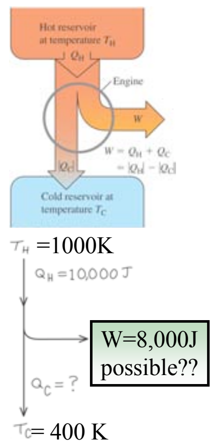
$$\Rightarrow 0 = -\frac{Q_h}{T_h} + \frac{Q_c^{min.}}{T_c} \Rightarrow \frac{Q_c^{min.}}{Q_h} = \frac{T_c}{T_h}$$

Minimum $Q_c \Rightarrow$ Maximum $W = Q_h - Q_c^{min.}$

$$\Rightarrow \text{Max. e} = \frac{W^{max}}{Q_h} = \frac{Q_h - Q_c^{min.}}{Q_h}$$

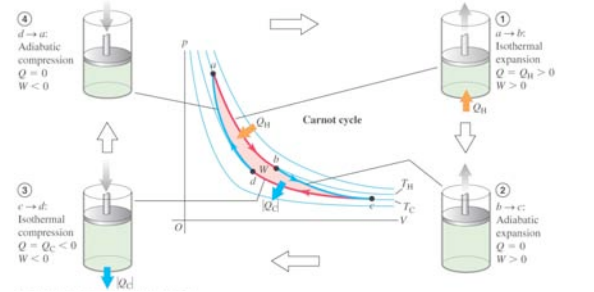
$$= 1 - \frac{Q_c^{min.}}{Q_h} = 1 - \frac{T_c}{T_h}$$

Note: The most efficient engine occurs when $\Delta S_{total} = 0$ => a reversible engine.



How can we achieve the "reversible", the most efficient engine?

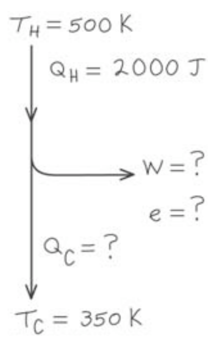
- The most efficient engine can be achieved with the "Carnot cycle".
- Carnot cycle consists of 4 segments: isothermal expansion, adiabatic expansion, isothermal compression, then finally adiabatic compression.



Analysis of Carnot Cycles

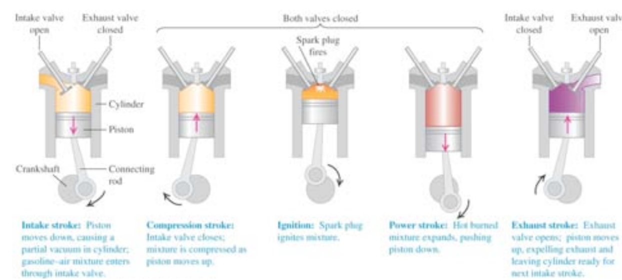
Find the values indicated in the figure.

Note; In order to achieve max. efficiency, the high temperature of the Carnot cycle must equal to the temperature of the hot reservoir, and the cold temperature of the Carnot cycle must equal to the temperature of the cold reservoir.
⇒heat flow is extremely slow (in fact no heat flow)
=> most efficient engine is the slowest engine!!



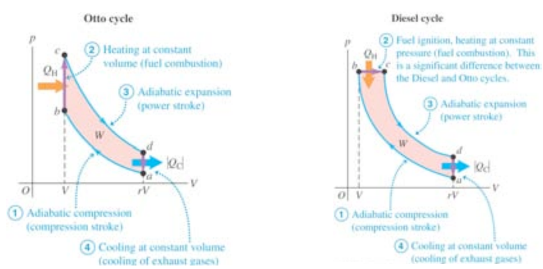
Real Engine - The internal-combustion engine

- A fuel vapor can be compressed, then detonated to rebound the cylinder, doing useful work.



Real engine cycles -The Otto cycle and the Diesel cycle

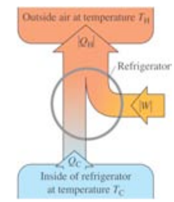
- A fuel vapor can be compressed, then detonated to rebound the cylinder, doing useful work.

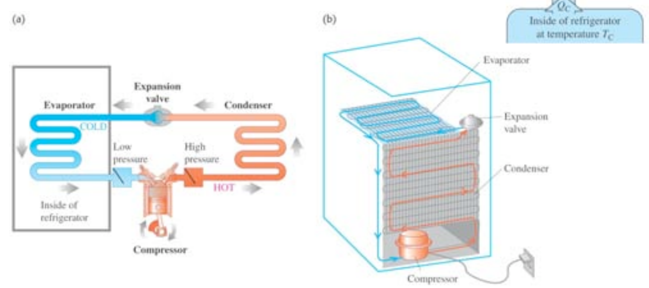


"Irreversible"=> cannot reverse the arrows WITHOUT changing the temperature of the reservoirs.

Refrigerators, air-conditioner, heat pumps

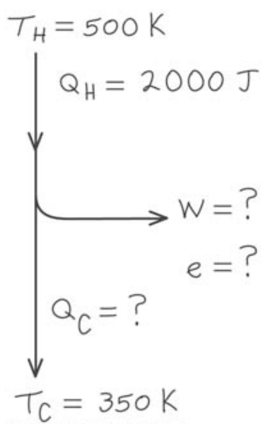
- A refrigerator, air-conditioner, or heat pump, are essentially a heat engine running backwards.





Analysis of Carnot Refrigerator

- ***Reverse all the arrows in the diagram for a refrigerator.***



Optional: Entropy function for a monatomic ideal gas

This is NOT in your text.

Start with definition: $dS = \frac{dQ}{T}$

Apply First Law: $dQ = dU + dW = dU + PdV$

For monatomic gas: $dU = \frac{3}{2}NkdT \quad \& \quad P = \frac{NkT}{V}$

$$\Rightarrow dS = \frac{3}{2}Nk\frac{dT}{T} + Nk\frac{dV}{V}$$

$$\int_i^f dS = \int_i^f \frac{3}{2}Nk\frac{dT}{T} + Nk\frac{dV}{V}$$

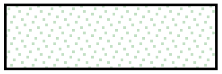
$$S_f - S_i = \frac{3}{2}Nk\ln\frac{T_f}{T_i} + Nk\ln\frac{V_f}{V_i}$$

$\Rightarrow S(N,T,V)$ is a state variable. You calculate the entropy of the system, once you know N,T,V.

In an abrupt processes, entropy changes without heat transfer

Entropy can change without heat transfer in an abrupt processes such as free-expansion of a gas, as illustrated below.

initial state

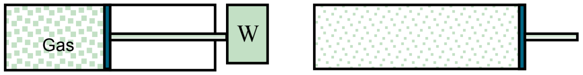


final state after partition is removed

In a "free-expansion" W=0 and Q=0, hence $U_f=U_i$.
One cannot calculate dS using dS=dQ/T in this abrupt process.
ΔS can be calculate from knowing entropy function.
ΔS>0 (initially the gas is "orderly" confined in a smaller volume, the final state is more disorder because the gas can be anywhere in a larger volume)

Entropy Change for slow expansion

If we expand the gas slowly by attaching a piston for the gas to do work (required heat input), then entropy change is again given by: dS=dQ/T



In this process heat is added in order to do work and keep U constant.
$S_f-S_i=\Delta S=Q/T>0$