EPFL

Thermodynamics of Earth systems

Lecture 5:

Entropy, the Second Law of Thermodynamics (continued)

Material covered in Lecture 5

Part 2: Framework

First Law of thermodynamics

- Basic concepts & processes
- Work; expansion work
- Heat: heat capacity, basics of heat transfer mechanisms
- First law: internal energy, enthalpy, specific heats, heat capacity.
- Applications of first law to ideal gases

Entropy and the 2nd law

- Entropy: reversible and irreversible processes; Clausius inequality; Boltzmann-Gibbs statistical picture of entropy
- Heat engines, Carnot Cycle and the maximum efficiency
- Applications of heat engines and Carnot Efficiency to atmosphere, ocean and deep earth
- 2nd Law of thermodynamics
- First and second laws combined
- Energy functions; Maxwell Equations

Heat engine

device which extracts work as thermal energy flows from a hot reservoir to a cold reservoir.

- external combustion engines

  (e.g. steam or Stirling engine)

- internal combustion engine

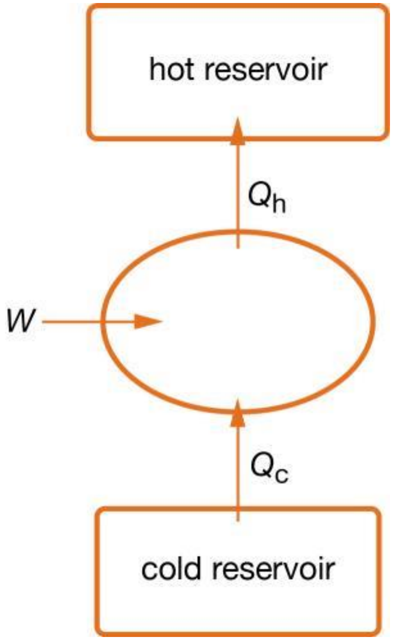
  (e.g. petrol or diesel engine, jet engine)

- refrigerators

- Clouds and weather systems

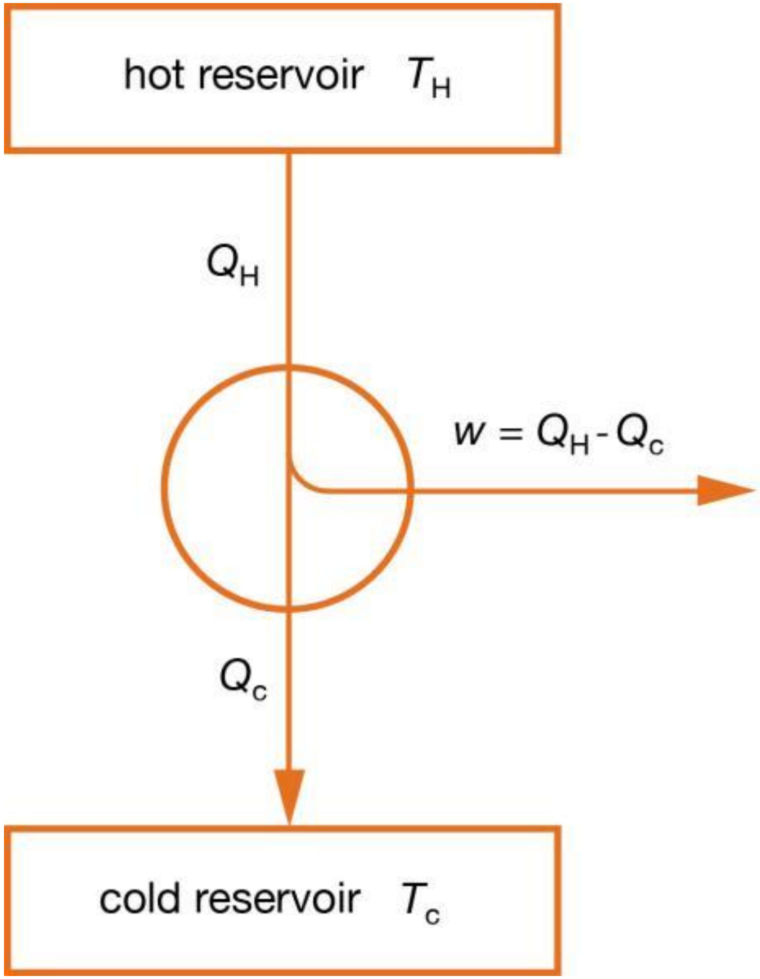
  (convective clouds, hurricanes)

- Many other types



Efficiency of a heat engine

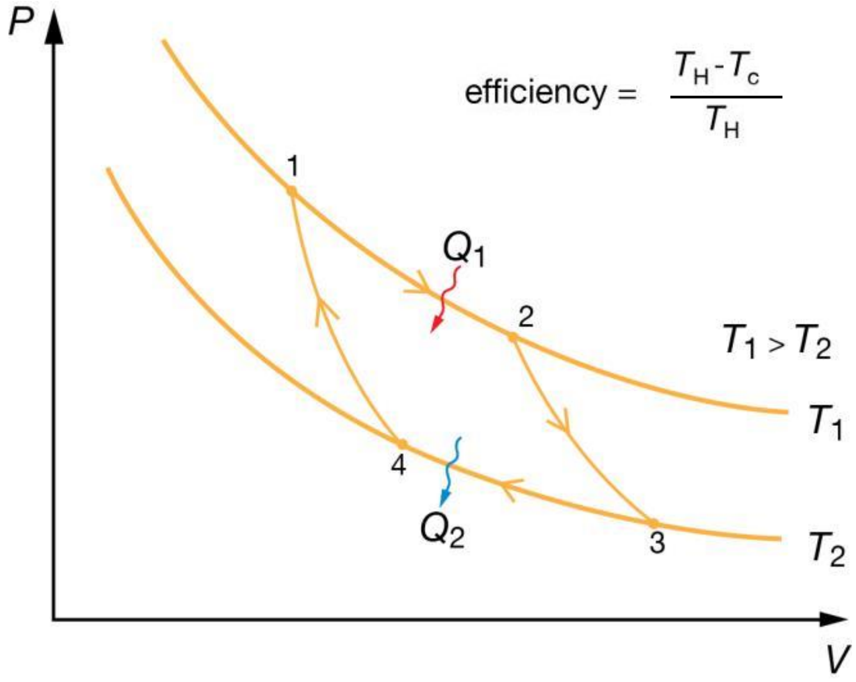
The efficiency of a Heat engine depends on the temperatures of the hot and cold reservoirs (Carnot)



Carnot cycle: Maximum efficiency

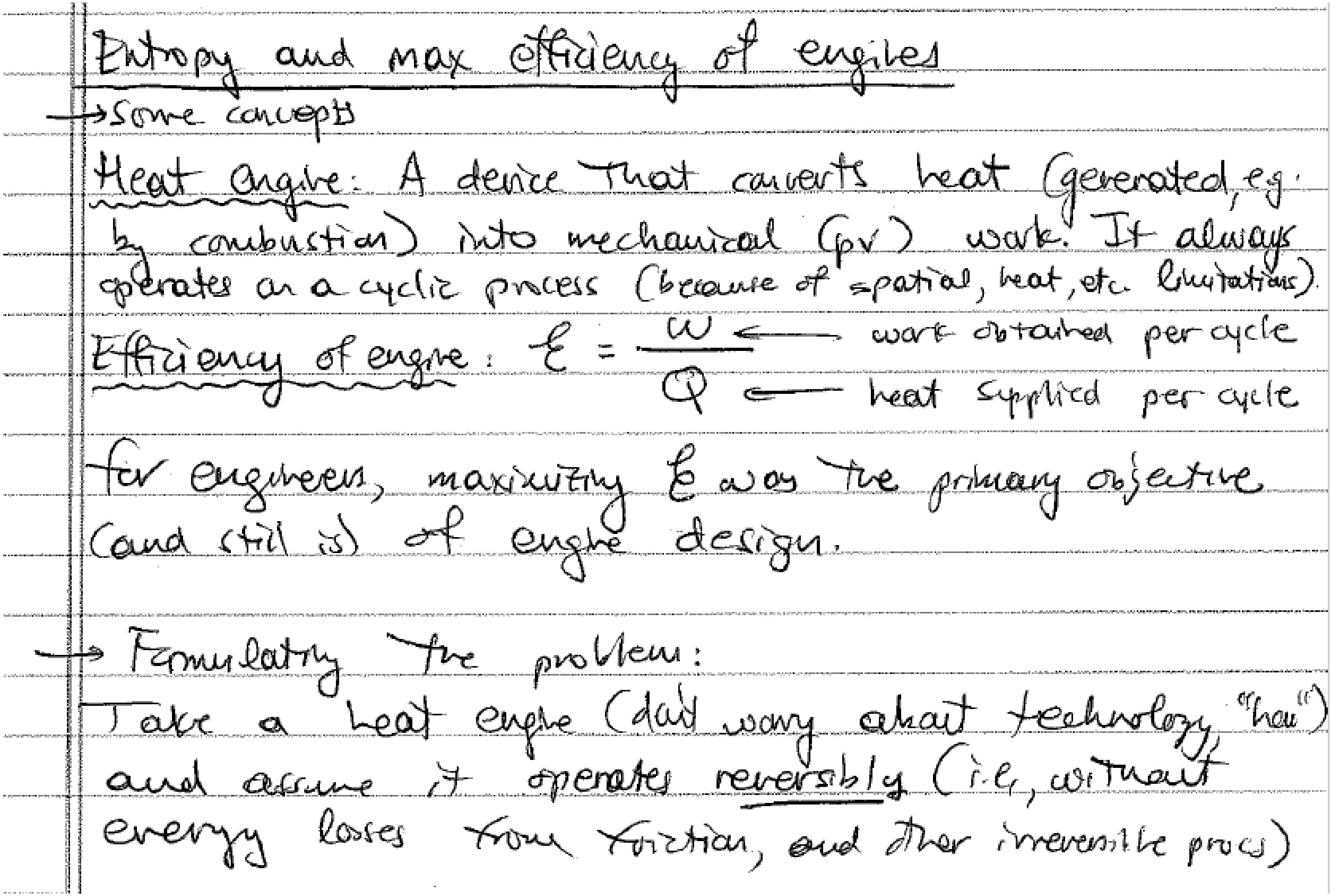
proposed by Carnot in 1824.

- most efficient cycle for an engine, converting a given amount of thermal energy into work
- most efficient cycle for a refrigerator, creating a ΔT (pumping the maximum heat) by doing a given amount of work.



It is the cycle for which $\Delta S_{\text{universe}} = 0$. It cannot get better than that. Other cycles tend to have $\Delta S_{\text{universe}} > 0$ so are less efficient.

Carnot cycle: Maximum efficiency



Entropy and max efficiency of engines

→ Some concepts

Heat engine: A device that converts heat (generated, e.g. by combustion) into mechanical (pV) work. It always operates on a cyclic process (because of spatial, heat, etc. limitations).

Efficiency of engine: $\varepsilon = \frac{W}{Q}$

W ← work obtained per cycle

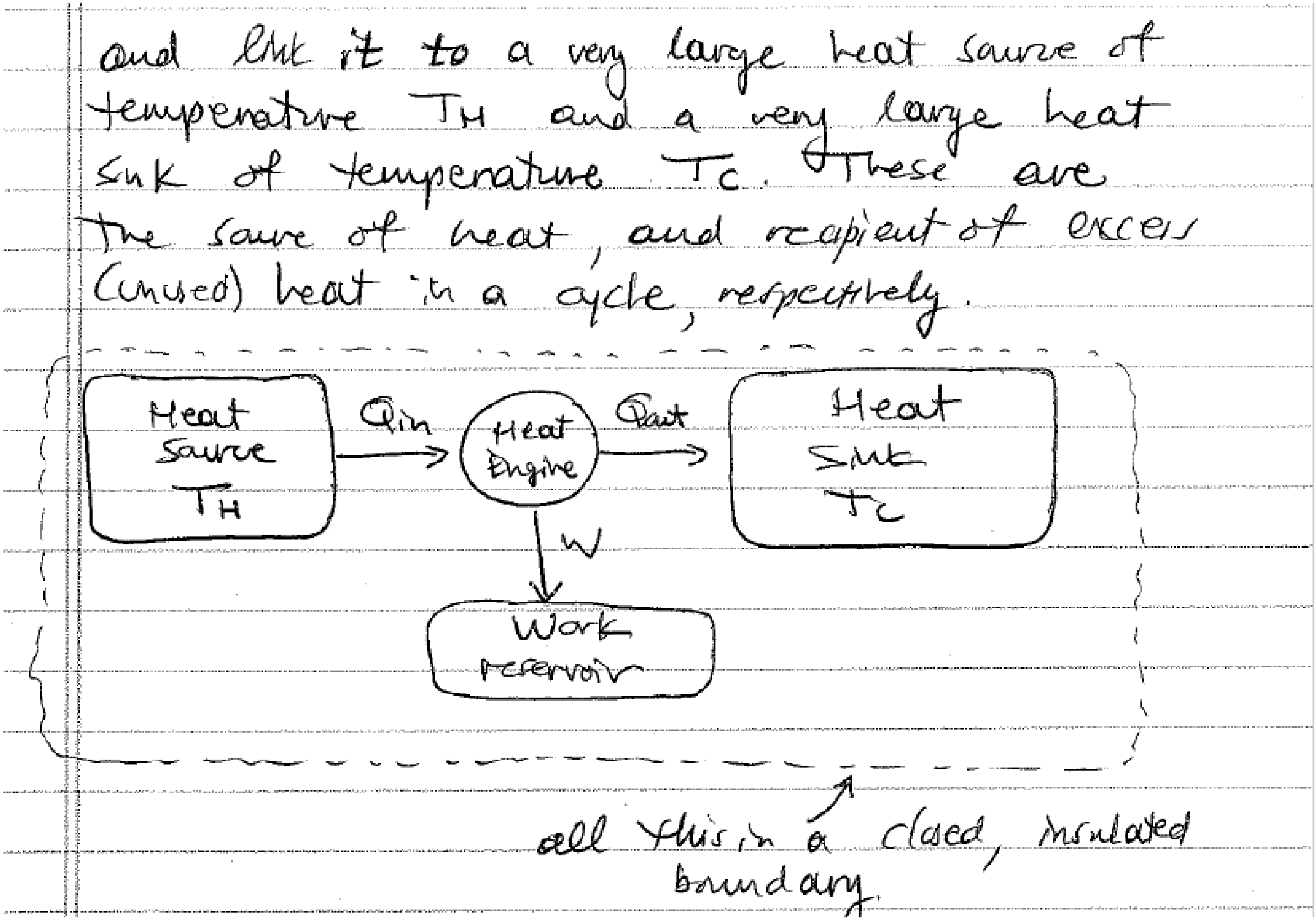
Q ← heat supplied per cycle

For engineers, maximizing ε was the primary objective (and still is) of engine design.

→ Formulating the problem:

Take a heat engine (don't worry about technology "how") and assume it operates reversibly (i.e., without energy losses from friction, and other irreversible procs)

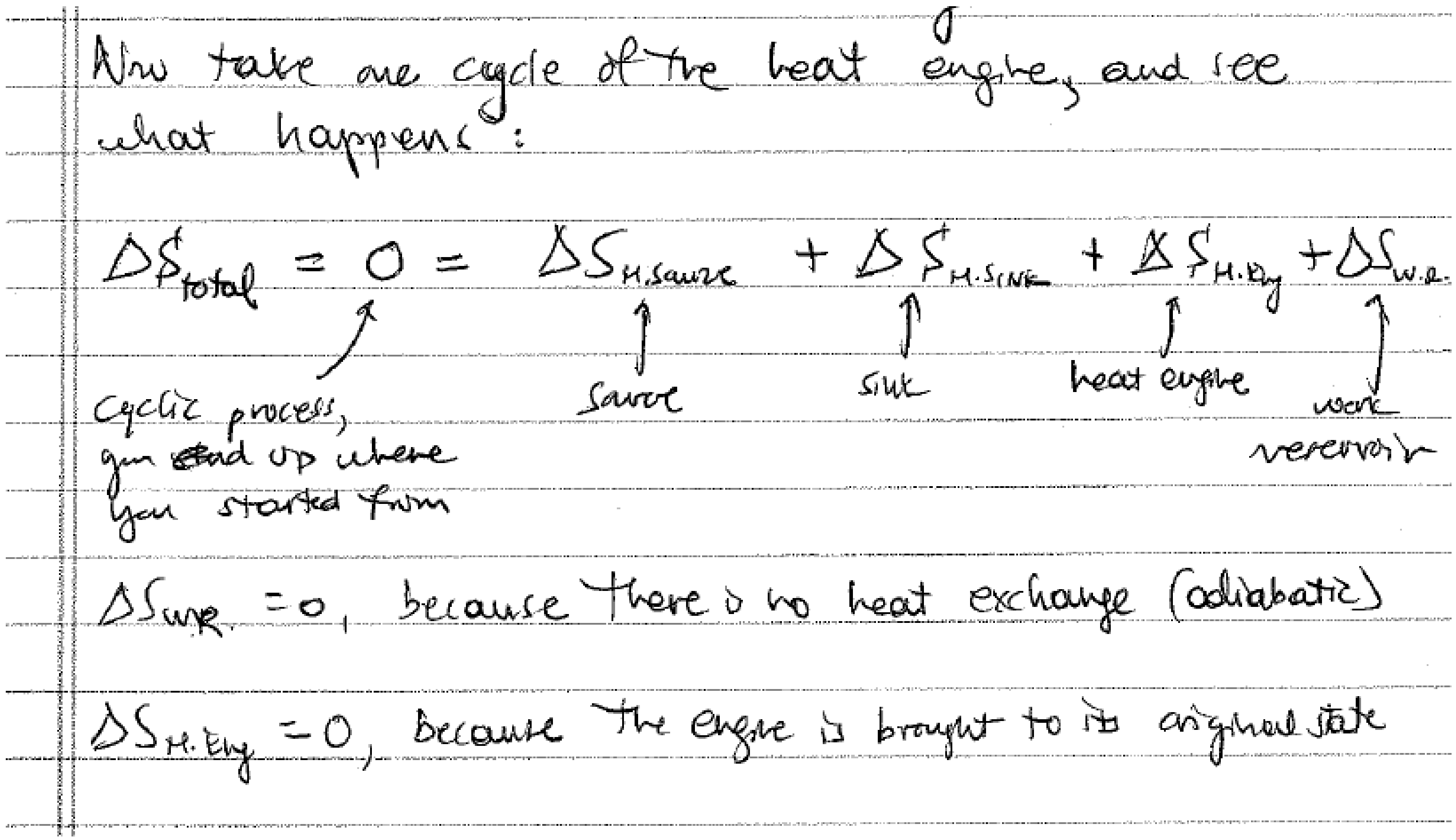
Carnot cycle: Maximum efficiency



and link it to a very large heat source of temperature T_H and a very large heat sink of temperature T_C. These are the source of heat, and recipient of excess (unused) heat in a cycle, respectively.

all this in a closed, insulated boundary.

Carnot cycle: Maximum efficiency



Now take one cycle of the heat engine, and see what happens:

$$\Delta S_{total} = 0 = \Delta S_{H.source} + \Delta S_{H.sink} + \Delta S_{H.Eng} + \Delta S_{W.R.}$$

cyclic process, you end up where you started from

source

sink

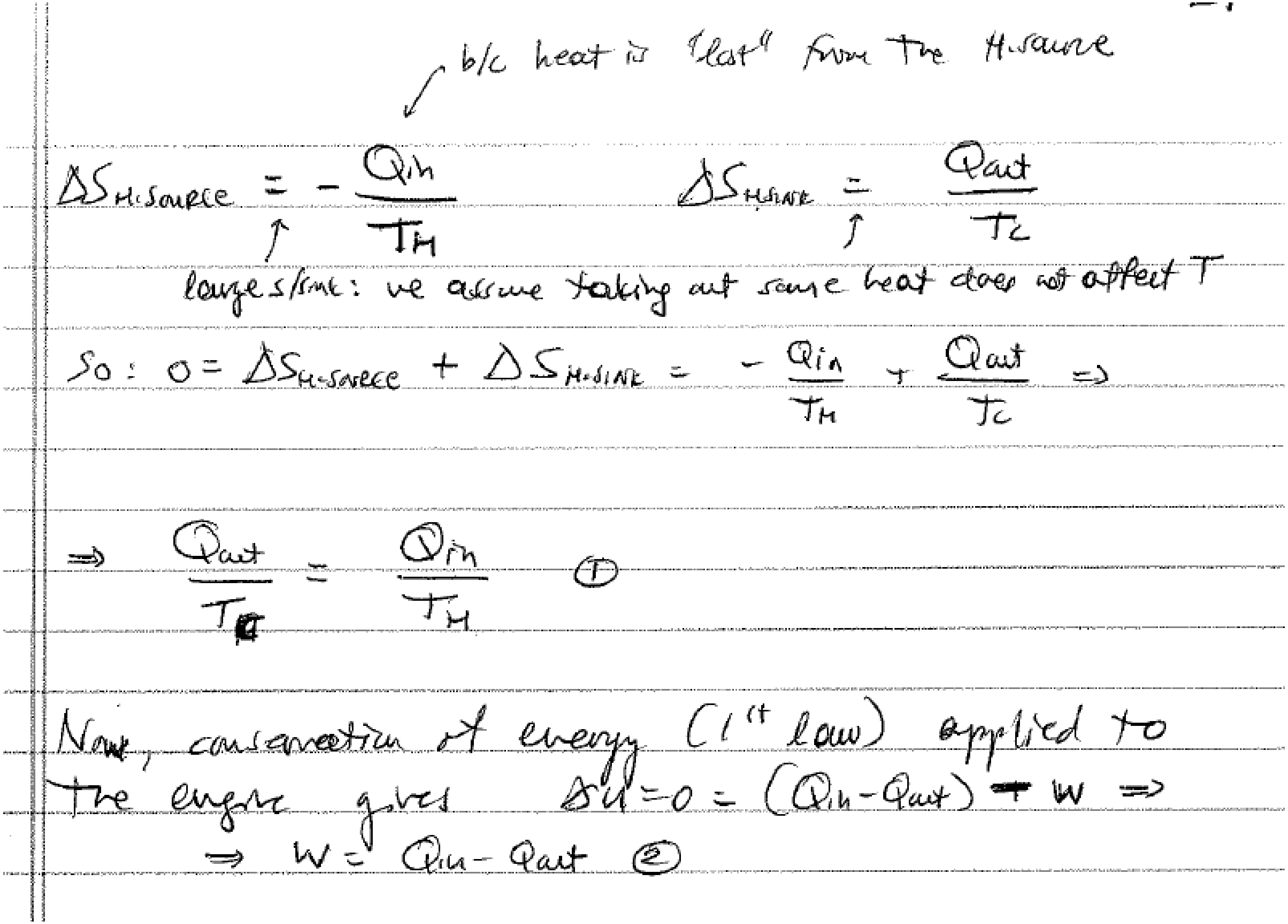
heat engine

work reservoir

$\Delta S_{W.R.} = 0$, because there is no heat exchange (adiabatic)

$\Delta S_{H.Eng} = 0$, because the engine is brought to its original state

Carnot cycle: Maximum efficiency



b/c heat is "lost" from the H-source

$\Delta S_{H\text{-}source} = -\frac{Q_{in}}{T_H}$ $\Delta S_{H\text{-}sink} = \frac{Q_{out}}{T_C}$

large s/snk: we assume taking out same heat does not affect T

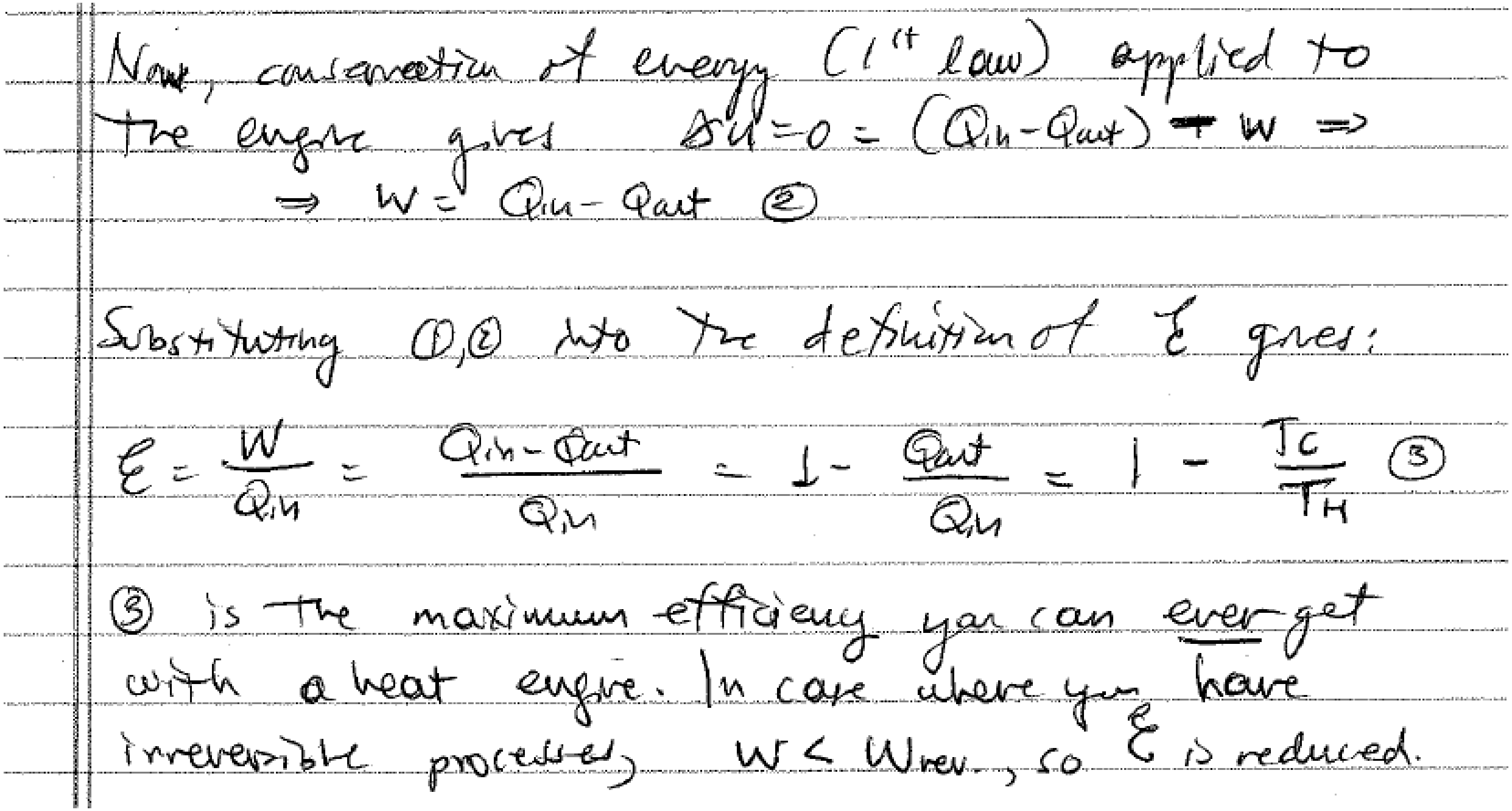
So: $0 = \Delta S_{H\text{-}source} + \Delta S_{H\text{-}sink} = -\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_C} \Rightarrow$

$$\Rightarrow \frac{Q_{out}}{T_C} = \frac{Q_{in}}{T_H} \quad ①$$

Now, conservation of energy (1st law) applied to the engine gives $\Delta U = 0 = (Q_{in} - Q_{out}) - W \Rightarrow$

$$\Rightarrow W = Q_{in} - Q_{out} \quad ②$$

Carnot cycle: Maximum efficiency



Now, conservation of energy (1st law) applied to the engine gives $\Delta U = 0 = (Q_{in} - Q_{out}) - W \Rightarrow$

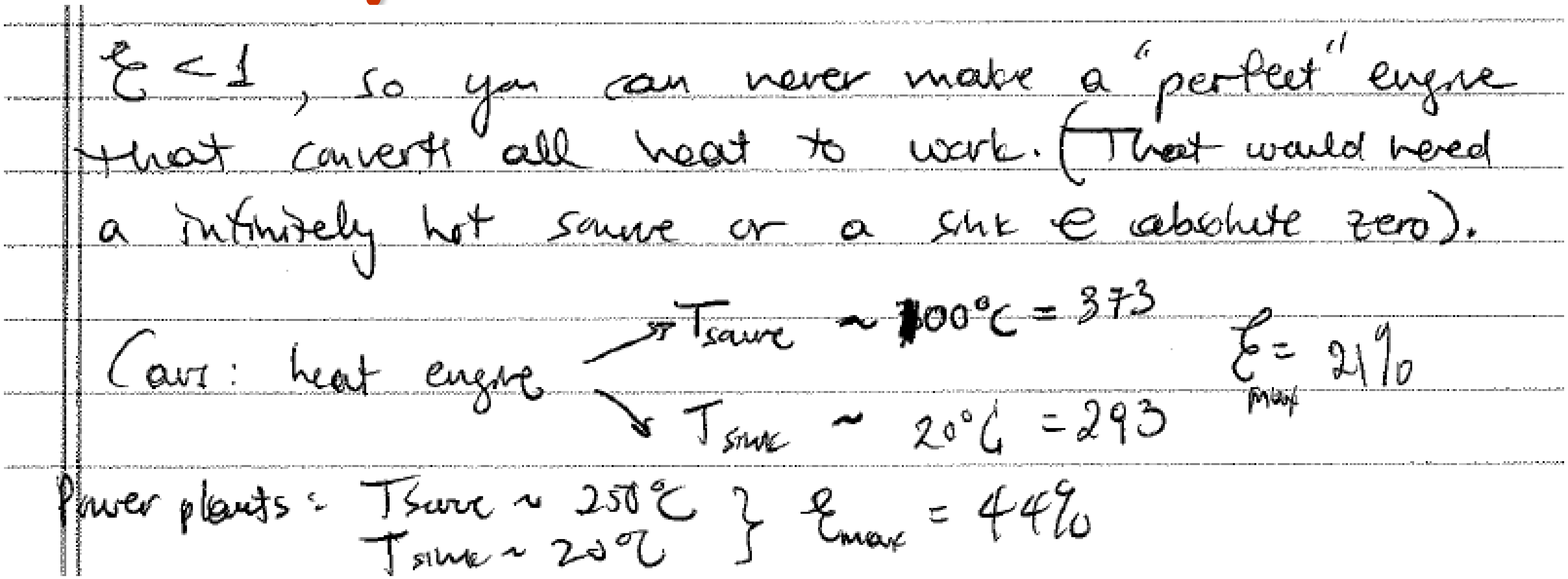
$\Rightarrow W = Q_{in} - Q_{out}$ ②

Substituting ①,② into the definition of $\mathcal{E}$ gives:

$$\mathcal{E} = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_C}{T_H} \quad ③$$

③ is the maximum efficiency you can <u>ever</u> get with a heat engine. In case where you have irreversible processes, $W < W_{rev.}$, so $\mathcal{E}$ is reduced.

Carnot cycle: Maximum efficiency

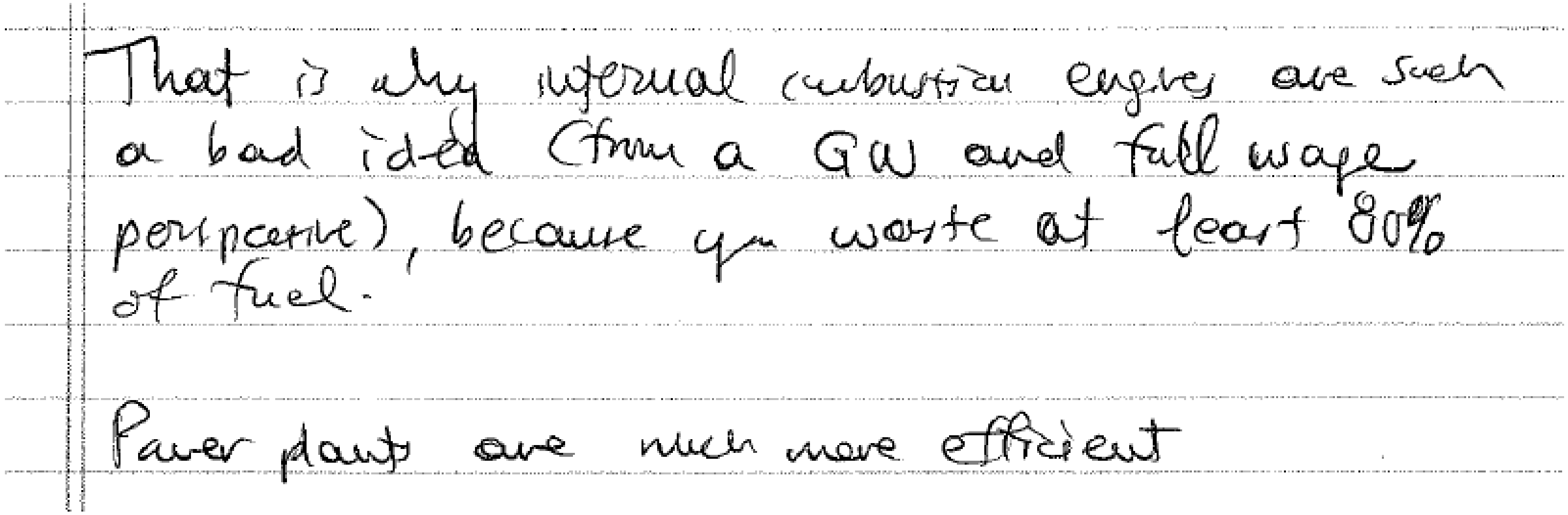


$\varepsilon < 1$, so you can never make a "perfect" engine that converts all heat to work. (That would need a infinitely hot source or a sink @ absolute zero).

Cars: heat engine
$\nearrow T_{\text{source}} \sim 100^\circ C = 373$
$\searrow T_{\text{sink}} \sim 20^\circ C = 293$

$\varepsilon_{\max} = 21\%$

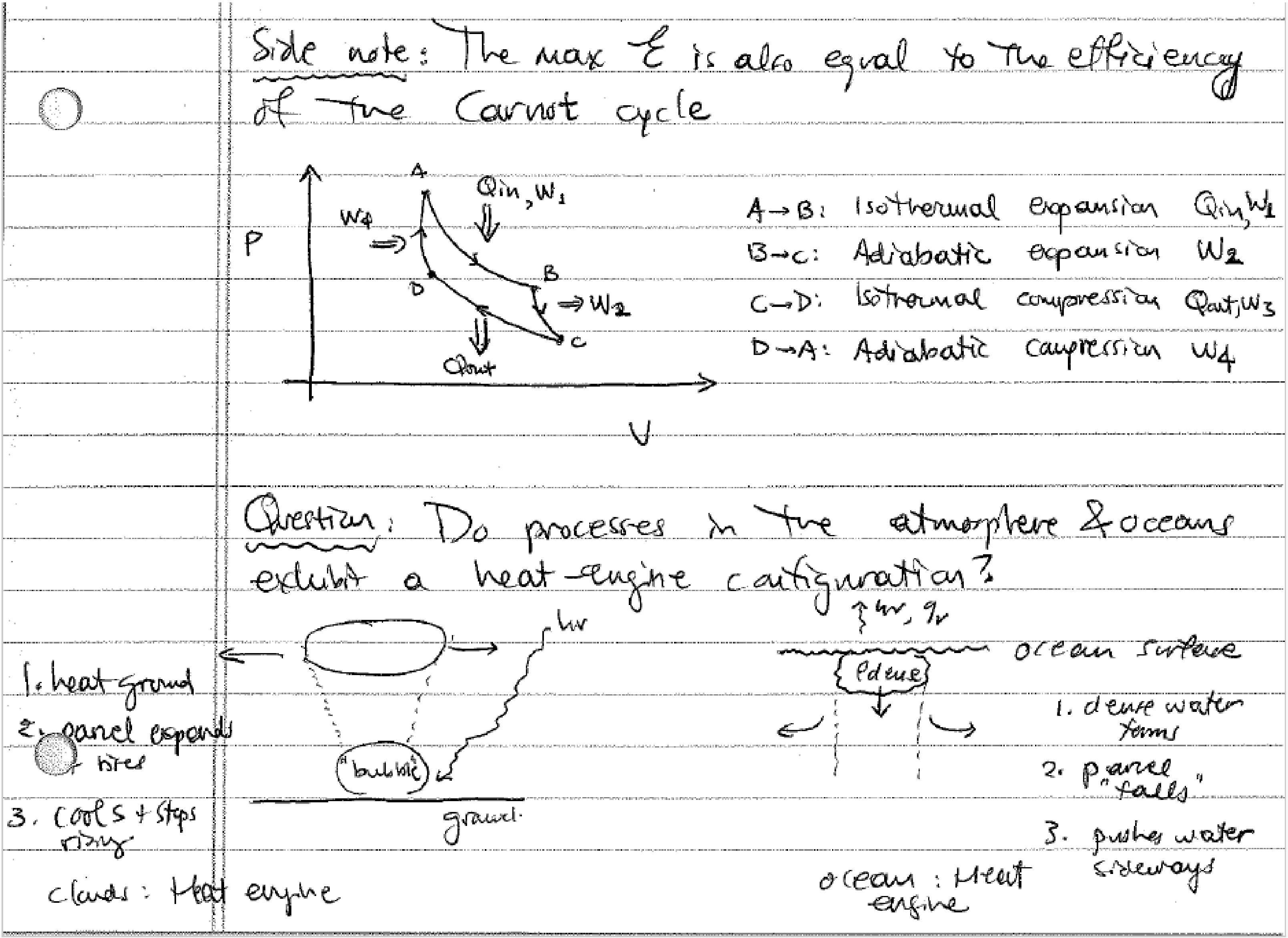
$$\text{Power plants: } \left.\begin{array}{l} T_{\text{source}} \sim 250^\circ C \\ T_{\text{sink}} \sim 20^\circ C \end{array}\right\} \varepsilon_{\max} = 44\%$$



That is why internal combustion engines are such a bad idea (from a GW and fuel usage perspective), because you waste at least 80% of fuel.

Power plants are much more efficient

Carnot cycle: Maximum efficiency



Side note: The max ε is also equal to the efficiency of the Carnot cycle

A→B:	Isothermal	expansion	Q_{in}, W_1
B→C:	Adiabatic	expansion	W_2
C→D:	Isothermal	compression	Q_{out}, W_3
D→A:	Adiabatic	compression	W_4

Question: Do processes in the atmosphere & oceans exhibit a heat-engine configuration?

1. heat ground
2. parcel expands + rises
3. cools + stops rising

clouds: Heat engine

1. dense water forms
2. parcel "falls"
3. pushes water sideways

ocean: Heat engine

Hurricanes as a Carnot Engine

quick study

Hurricanes: Tempests in a greenhouse

Kerry Emanuel

Greenhouse gases make Earth's surface hotter than it would be if the planet were simply a blackbody radiator. That additional warming is an important driver of hurricanes.

Kerry Emanuel is a professor of atmospheric sciences at the Massachusetts Institute of Technology in Cambridge, Massachusetts.

The tropics have generally the most benign climates found on Earth, with gentle breezes and small daily and seasonal temperature variations. Why, then, do tropical climates breed the most destructive wind storms known? This brief tutorial explains the paradox and presents an overview of hurricane physics.

The greenhouse effect

Of the solar energy that streams to Earth, about 30% is reflected by clouds or the surface, and an additional small percentage is directly absorbed by atmospheric water—either gaseous or condensed in clouds. The radiation that escapes reflection or absorption in the atmosphere is absorbed by the surface, which transmits energy upward both by radiation and in vast convective currents whose visible manifestations are the beautiful cumulus and cumulonimbus clouds that ply the tropical skyscape. The outgoing photons have much longer wavelengths than the incoming photons, since Earth's surface temperature is far lower than the Sun's. The outgoing IR radiation is strongly absorbed by clouds and by trace amounts of certain gaseous components of the atmosphere, notably water vapor, carbon dioxide, and methane. Those constituents reradiate both upward and downward. Remarkably, the surface receives on average more radiation

ated with precipitation absorb most of the entropy production and spare people from violent winds. But not always.

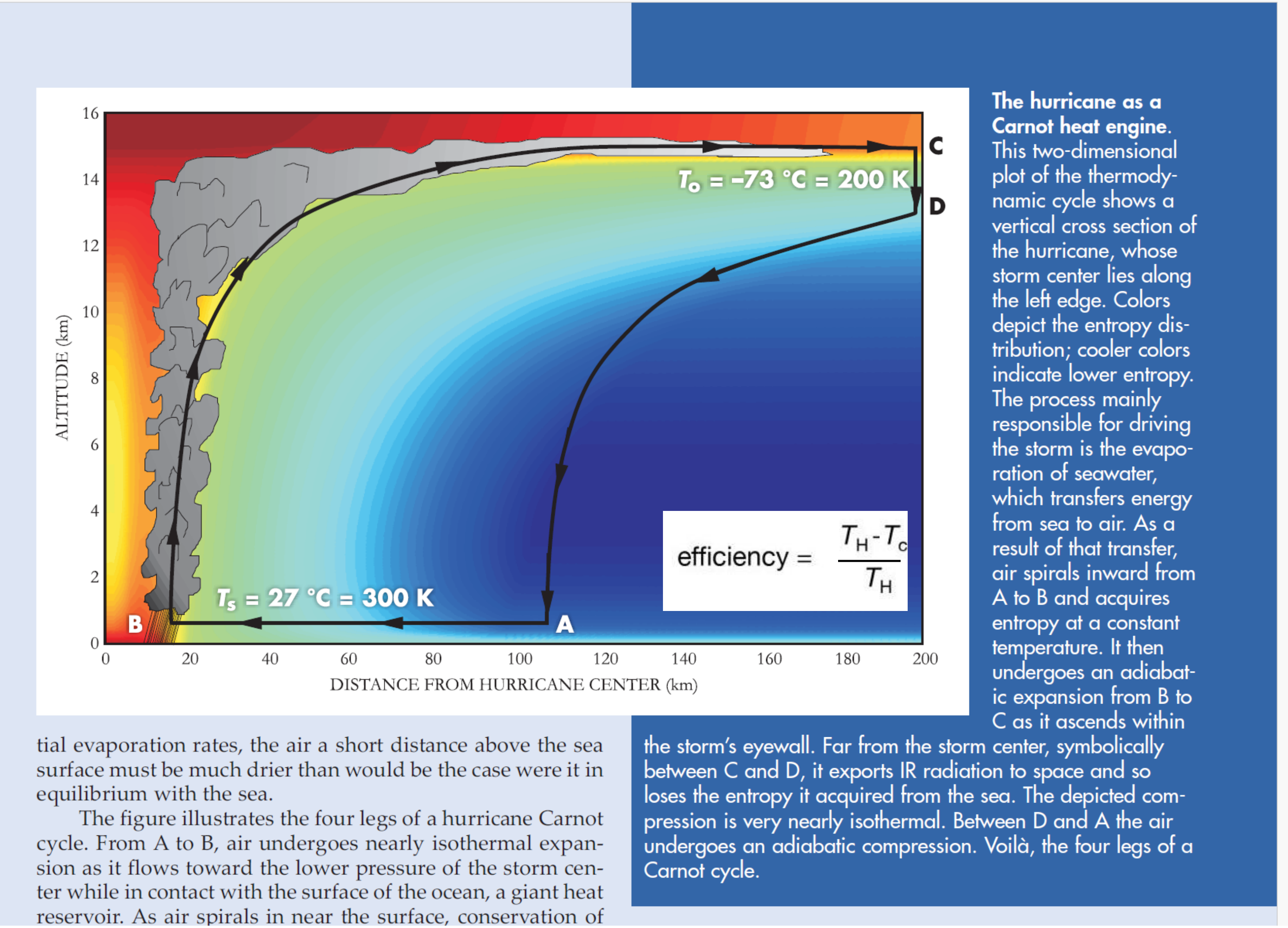
A Carnot engine

In the part of the tropics where the sea surface is warm enough and the projection of Earth's angular velocity vector onto the local vertical axis is large enough, random small-scale convective currents sometimes organize into rotating vortices known as tropical cyclones. In computer models of the tropical atmosphere, such organization can happen spontaneously, but usually only if a combination of ocean temperature and rotation is somewhat higher than those observed in nature. In subcritical conditions, some trigger is necessary to initiate the vortices, and in the terrestrial atmosphere tropical cyclones only develop from preexisting disturbances of independent origin. In mathematical parlance, tropical cyclones may be said to result from a subcritical bifurcation of the radiative–convective equilibrium state. About 10% of them develop in the Atlantic Ocean, where the disturbance is often a 100-km-scale "easterly wave" that forms over sub-Saharan Africa and then moves westward out over the Atlantic. When its maximum wind speed exceeds 32 m/s, it, by definition, becomes a hurricane.

The convective core of a tropical cyclone may be many

Manuscript in reading material (2 pages)

Hurricanes as a Carnot Engine



$$\text{efficiency} = \frac{T_H - T_c}{T_H}$$

The hurricane as a Carnot heat engine. This two-dimensional plot of the thermodynamic cycle shows a vertical cross section of the hurricane, whose storm center lies along the left edge. Colors depict the entropy distribution; cooler colors indicate lower entropy. The process mainly responsible for driving the storm is the evaporation of seawater, which transfers energy from sea to air. As a result of that transfer, air spirals inward from A to B and acquires entropy at a constant temperature. It then undergoes an adiabatic expansion from B to C as it ascends within the storm's eyewall. Far from the storm center, symbolically between C and D, it exports IR radiation to space and so loses the entropy it acquired from the sea. The depicted compression is very nearly isothermal. Between D and A the air undergoes an adiabatic compression. Voilà, the four legs of a Carnot cycle.

tial evaporation rates, the air a short distance above the sea surface must be much drier than would be the case were it in equilibrium with the sea.

The figure illustrates the four legs of a hurricane Carnot cycle. From A to B, air undergoes nearly isothermal expansion as it flows toward the lower pressure of the storm center while in contact with the surface of the ocean, a giant heat reservoir. As air spirals in near the surface, conservation of

The Laws of Thermodynamics

0. Two bodies in thermal equilibrium are at same T
1. Energy can never be created or destroyed.

$$\Delta E = q + w$$

2. The total entropy of the UNIVERSE (= system plus surroundings) MUST INCREASE in every spontaneous process.

$$\Delta S_{TOTAL} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

3. The entropy (S) of a pure, perfectly crystalline compound at T = 0 K is ZERO. (no disorder)

$S_{T=0} = 0$ (perfect xll)

Life and the second law

Schrodinger (1943) What is life?

‘Life’s ability to maintain itself, expand, and reproduce in a world subject to the second law is a paradox explained by the fact that live beings, open to and dependent upon energy via light or chemical reactions, release heat and other thermodynamic wastes into their environment. … Their high organisation and low entropy is made up for by pollution, heat, and entropic export to their surroundings.’ E Schneider & D Sagan (2005)

Into the Cool: Energy flow, thermodynamics and life

‘Metabolism’ [*Greek*: meta, after + bole, change]

Sustaining life & entropy production

> ‘Gradients can be of pressure, chemical concentration, temperature or any work-related potential. As gradients move systems away from equilibrium, the systems shift states so as to oppose the applied gradients. In general, as systems move away from equilibrium, increasingly more energy is needed to keep them there.’

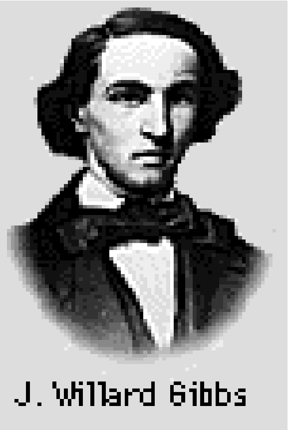
E Schneider & D Sagan (2005)

Into the Cool: Energy flow, thermodynamics and life

i.e.: Life helps bring more disorder to the universe.

A consequence of the second law?

Gibbs Free Energy


J. Willard Gibbs

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$$

$$\Delta S_{univ} = \frac{-\Delta H_{sys}}{T} + \Delta S_{sys}$$

Multiply through by -T

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

$-T\Delta S_{univ}$ = **change in Gibbs free energy for the system** = ΔG_{system}

Under standard conditions —

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

The Gibbs Equation

Sign of ΔG for Spontaneous processes

2nd LAW requirement for SPONTANEITY is :

$$\Delta S_{TOTAL} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

Multiply by T $T\Delta S_{system} + T\Delta S_{surroundings} > 0$

and $\Delta S_{surroundings} = \Delta H^o_{system}/T$

Thus $T\Delta S_{system} - \Delta H^o_{system} > 0$

Multiply by -1 (->reverse > to <), drop subscript “system”

→ $\Delta H^o - T\Delta S < 0$ **and** $\Delta G^o = \Delta H^o - T\Delta S$

→ $\Delta G^o < 0$ **for all SPONTANEOUS processes**

Sign of Gibbs Free Energy, ΔG

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

- **change in Gibbs free energy =**

  (total free energy change for system - free energy lost in disordering the system)

- **If reaction is exothermic (ΔH^o is -ve) and entropy increases (ΔS^o is +ve), then ΔG^o must be -ve and reaction CAN proceed.**

- **If reaction is endothermic (ΔH^o is +ve), and entropy decreases (ΔS^o is -ve), then**

  ΔG^o must be +ve; reaction CANNOT proceed.

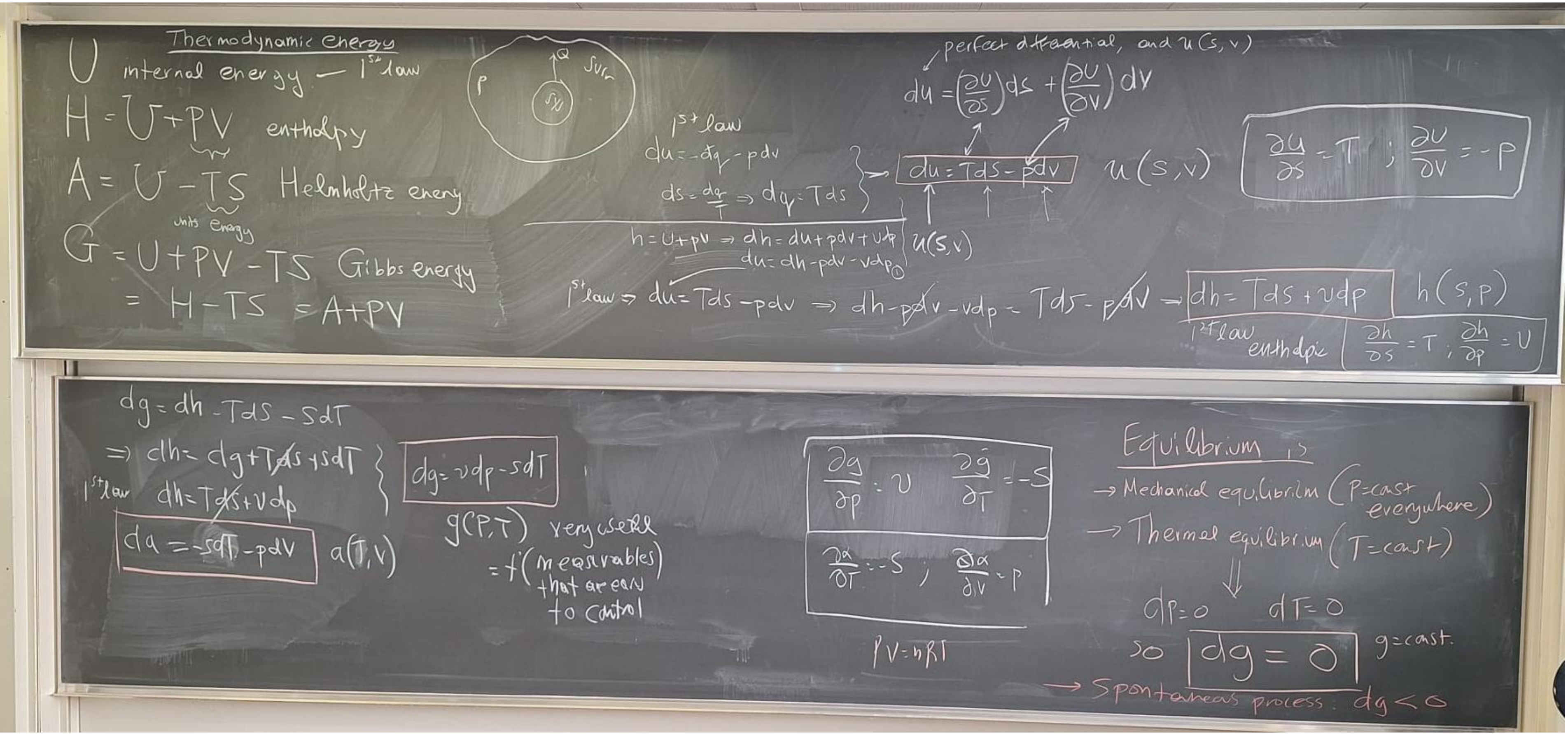
Gibbs Free Energy changes for reactions

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

ΔH^o	ΔS^o	ΔG^o	Reaction
exo (-)	increase(+)	-	Product-favored
endo(+)	decrease(-)	+	Reactant-favored
exo (-)	decrease(-)	?	T dependent
endo(+)	increase(+)	?	T dependent

Spontaneous in last 2 cases only if Temperature is such that $\Delta G^o < 0$

Thermodynamic functions



Thermodynamic energy

U internal energy — 1st law

$H = U + PV$ enthalpy

$A = U - TS$ Helmholtz energy

$\underbrace{TS}_{\text{units energy}}$

$G = U + PV - TS$ Gibbs energy

$= H - TS = A + PV$

1st law

$du = dq - pdv$

$ds = \frac{dq}{T} \Rightarrow dq = Tds$

$\boxed{du = Tds - pdv}$ $u(s,v)$

perfect differential, and $u(s,v)$

$du = \left(\frac{\partial u}{\partial s}\right) ds + \left(\frac{\partial u}{\partial v}\right) dv$

$\boxed{\frac{\partial u}{\partial s} = T \;;\; \frac{\partial u}{\partial v} = -p}$

$h = u + pv \Rightarrow dh = du + pdv + vdp$

$du = dh - pdv - vdp$ ①

$u(s,v)$

1st law $\Rightarrow du = Tds - pdv \Rightarrow dh - \cancel{pdv} - vdp = Tds - \cancel{pdv} \rightarrow \boxed{dh = Tds + vdp}$ $h(s,p)$

1st law enthalpic $\boxed{\frac{\partial h}{\partial s} = T \;;\; \frac{\partial h}{\partial p} = v}$

$dg = dh - Tds - sdT$

$\Rightarrow dh = dg + T\cancel{ds} + sdT$

1st law $dh = T\cancel{ds} + vdp$

$\boxed{dg = vdp - sdT}$

$g(P,T)$ very useful

$= f$(measurables that are easy to control)

$\boxed{da = -sdT - pdV}$ $a(T,V)$

$\boxed{\frac{\partial g}{\partial p} = v \quad \frac{\partial g}{\partial T} = -S}$

$\boxed{\frac{\partial a}{\partial T} = -S \;,\; \frac{\partial a}{\partial V} = -p}$

$PV = nRT$

Equilibrium is

→ Mechanical equilibrium (P = const everywhere)

→ Thermal equilibrium (T = const)

$\Downarrow$

$dp = 0 \quad dT = 0$

so $\boxed{dg = 0}$ g = const.

→ Spontaneous process: $dg < 0$

See notes for more details