Theories of Everything:
Thermodynamics
Statistical Physics
Quantum Mechanics

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> We are the proud owners of a set of mathematical relationships, that, as far as we know, account for everything in the natural world bigger than an atomic nucleus.

R.B. Laughlin, p. 4.

Thermodynamics

Jennings Conjecture

> Thus, $1 - T/T_r$ represents a kind of efficiency horizon beyond which negative entropy is produced and the second law is not obeyed. As this is impossible for a heat machine, it serves to underline the difference between photosynthetic photochemistry and a heat machine.

Jennnings *et al.*, BBA, 1709, (2005), 251.

> It is impossible to take heat from a reservoir and in a cyclic process completely convert it to work.

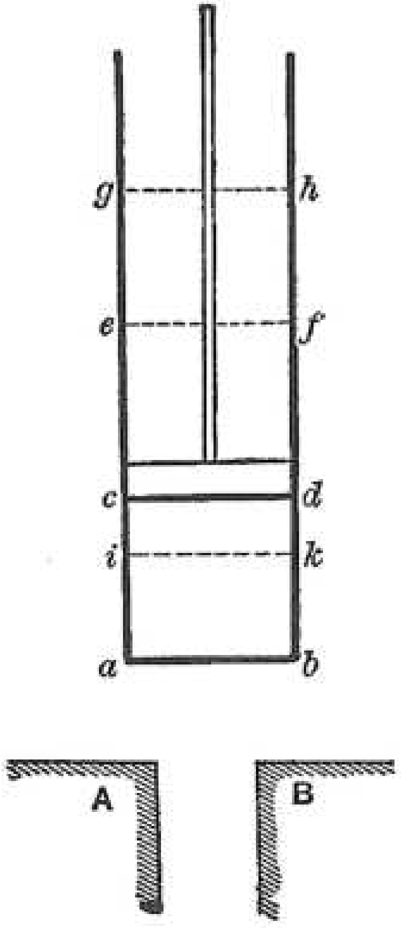
Lord Kelvin, 1851.

Thermodynamics and Life

> In fact it would seem reasonable to define life as being characterized by a capacity for evading this law. If probably cannot evade the laws of atomic physics, which are believed to apply as much to the atoms of a brain as to the atoms of a brick, but it seems able to evade this statistical laws of probability.

James Jeans, 1933.

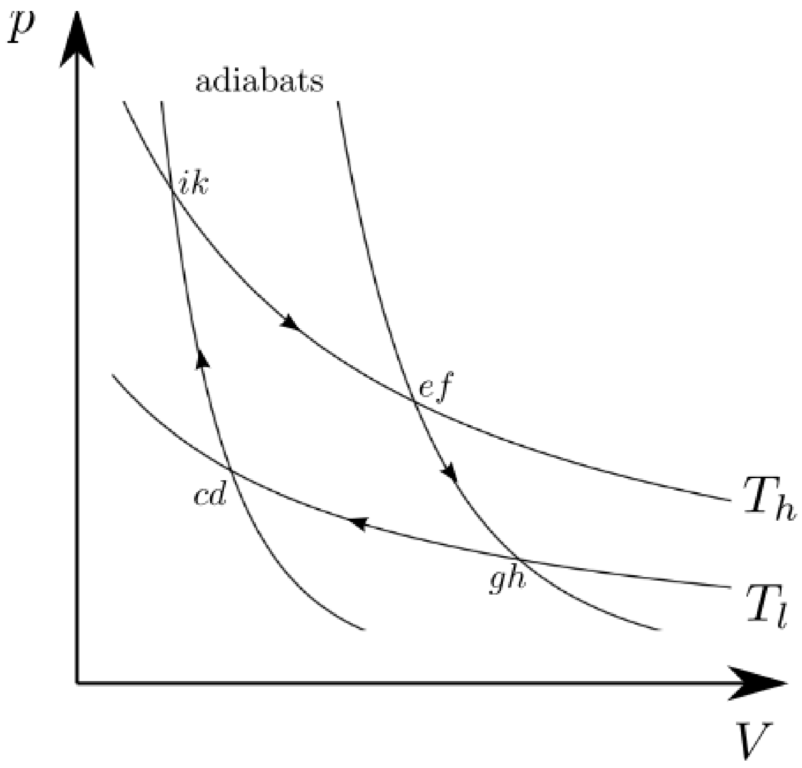
Carnot's Heat Engine



A is a hot and B a cold reservoir.

1. Isothermal expansion from ik to ef, while the cylinder is on A. Heat is converted to work.
2. Adiabatic expansion from ef to gh, while the cylinder is isolated. No heat is exchanged, work is performed.
3. Isothermal compression from gh to cd, while the cylinder is on B. Work is converted to heat.
4. Adiabatic compression from cd to the initial position.

p, V *Diagram for the Ideal Gas*

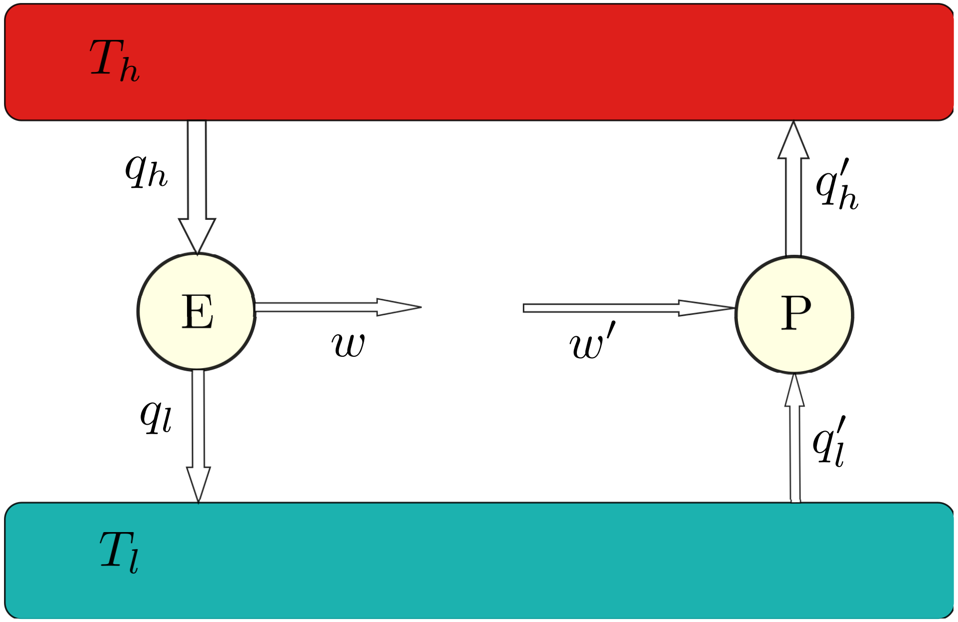


Tradiational Carnot diagram for the ideal gas with isotherms (marked T_l and T_h) and adiabatic curves.

Conclusions from Carnot's cycle.

- Once a cycle is completed the gas in the cylinder is in the same state as before.
- Once a cycle is completed a certain amount of heat taken from the high temperature reservoir has been converted to work.
- Once a cycle is completed a certain amount of heat is given off to the cold reservoir.
- All reversible engines have the same efficiency: $1 - \frac{T_B}{T_A}$.
- All other (heat?) engines are less efficient.
- There is a state quantity we will call **Entropy**.

Engines and Heat Pumps



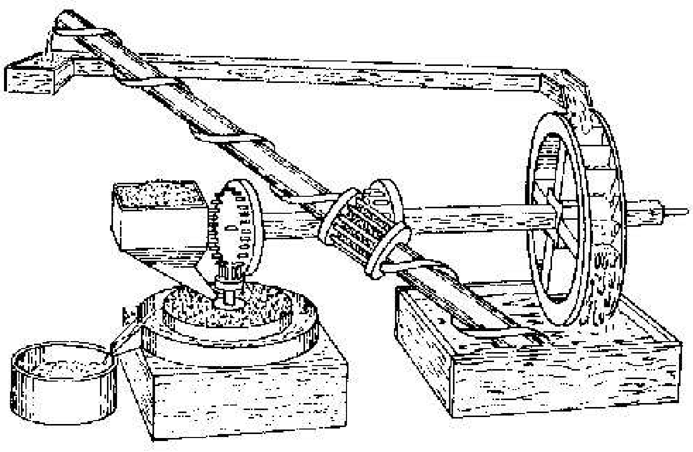
E is a reversible ‘Heat Machine’ and P a reversible heat pump.

$$q_h = w + q_l \quad q'_h = q'_l + w'$$

Efficiency

- Suppose E is more efficient than P: $w > w'$.
- We make $q_l = q_l'$ (can always be done).
- Then $q_h > q_h'$.

Final Effect: heat $q_h - q_h'$ is taken from high T reservoir, and completely converted to work $w - w'$.



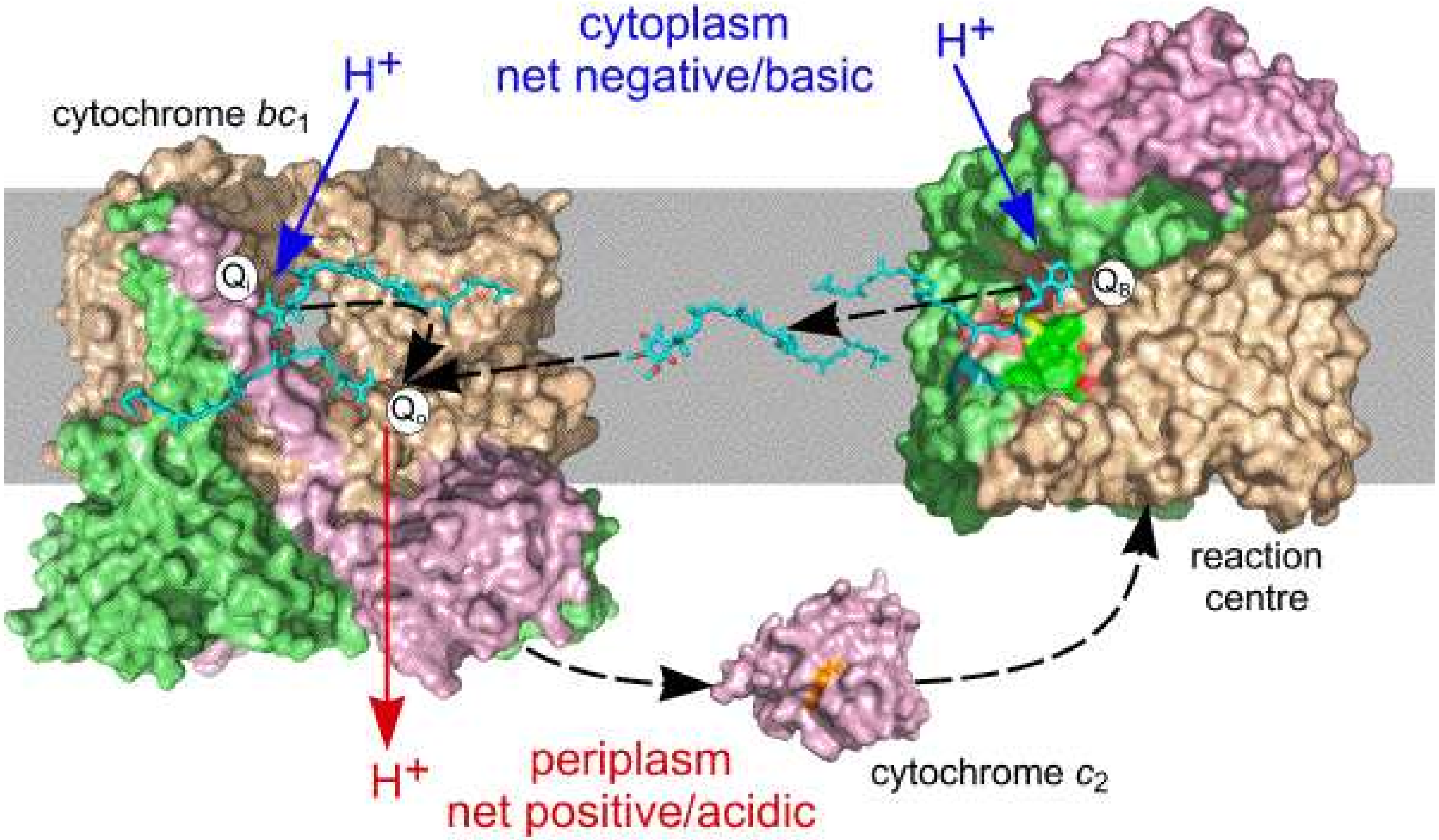
Just as you cannot take work from falling water and bring that back to the same level, you cannot take work from heat and bring that back to the same level.

Conclusions

1. All reversible Carnot machines are equally efficient (regardless of the medium they use).
2. All other machines are less efficient than reversible machines.

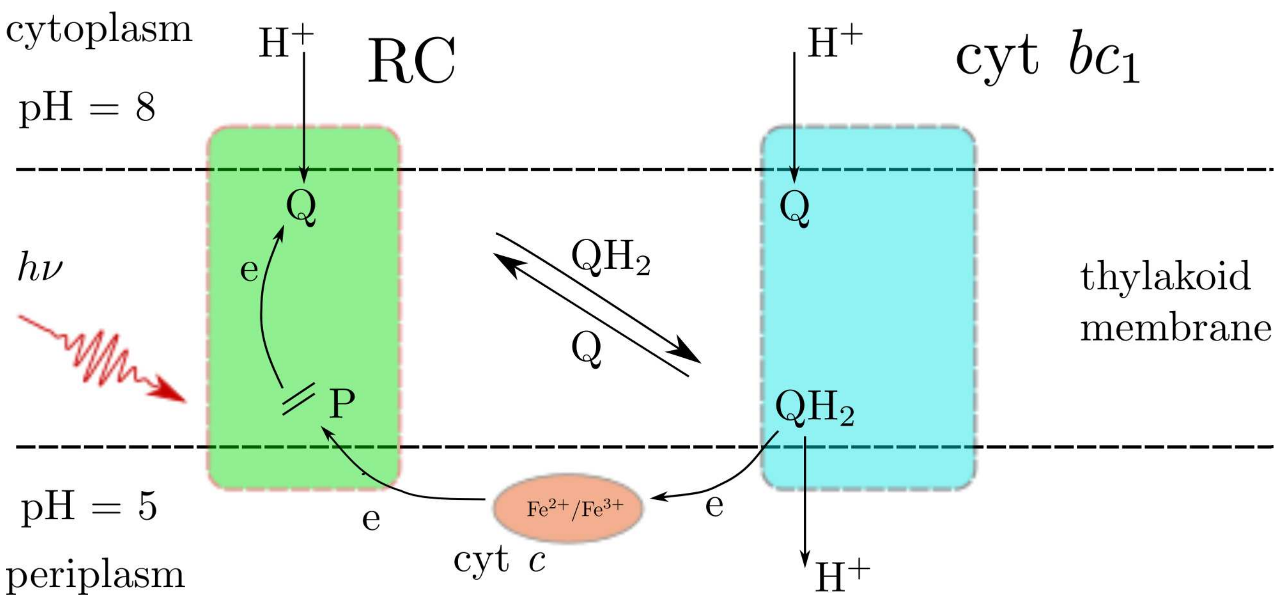
Jennings’ conjecture: Photosystems are perpetual motion machines of the second kind.

Bacterial Photosynthesis



Mike Jones, http://www.photobiology.info/Jones.html

Photosynthesis Simplified



All that bacterial photosynthesis accomplishes is the transport of protons over a membrane against the gradient. It performs work using heat from the photon. One 870 nm photon can transport two protons.

Heat, Work, and Entropy

- Work performed per two photons:

$$w = \Delta\mu = -2 \times 2.3 \times k_B T \Delta pH = 1.89 \times 10^{-20}\,\mathrm{J} \qquad (1)$$

- Heat taken from T_h:

$$q_h = \frac{hc}{\lambda} = 2.28 \times 10^{-19}\,\mathrm{J} \qquad (2)$$

- Heat dumped at low temperature (First law of Thermodynamics):

$$q_l = q_h - w = 2.09 \times 10^{-19}\,\mathrm{J} \qquad (3)$$

Heat, Work, and Entropy II

- Entropy change of the high temperature reservoir:

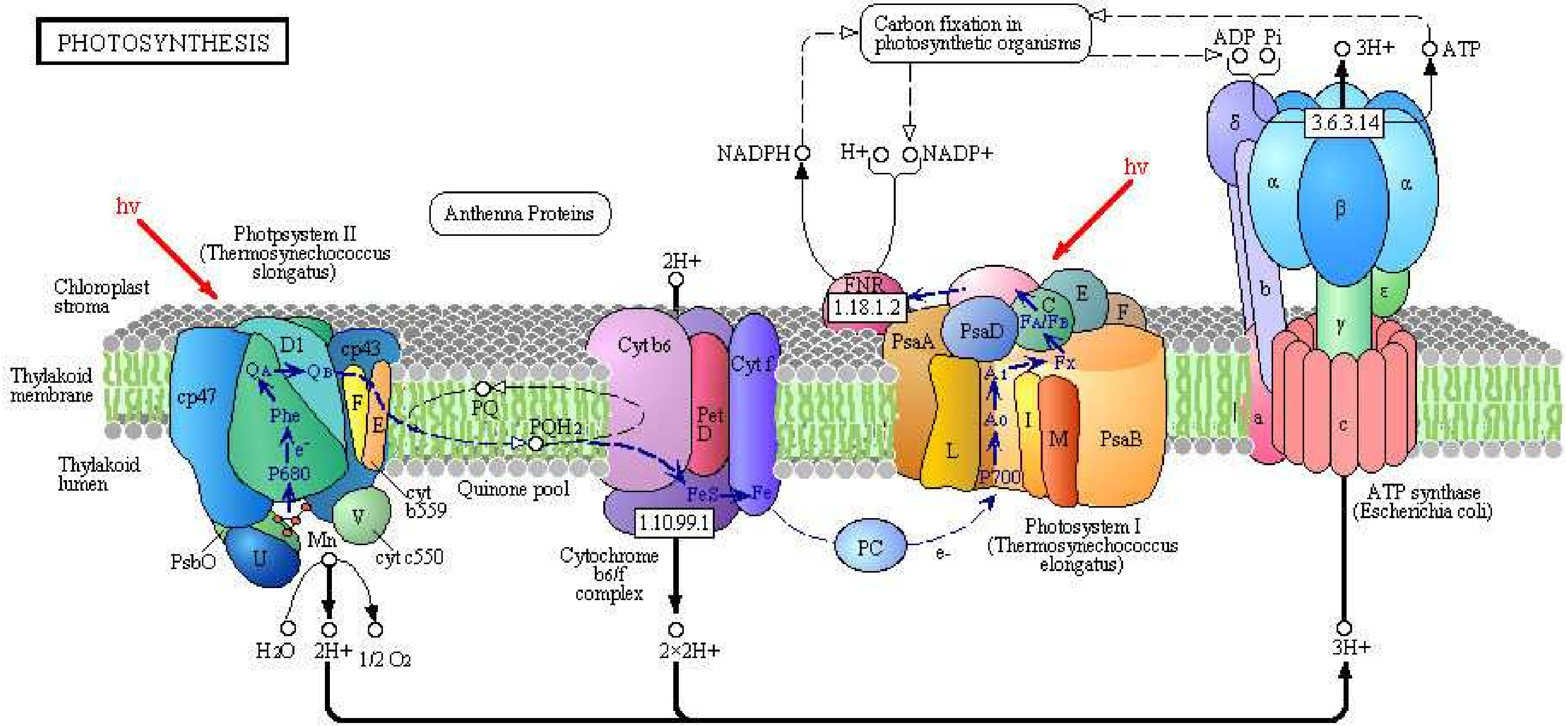
$$\Delta S_h = -\frac{2.28 \times 10^{-19}}{1100} = -3.8 \times 10^{-23}\,\mathrm{J/K} \qquad (4)$$

- Entropy change of the low temperature reservoir:

$$\Delta S_l = \frac{2.09 \times 10^{-19}}{300} = 7.9 \times 10^{-22}\,\mathrm{J/K} \qquad (5)$$

Total change of entropy: $\Delta_{\mathrm{tot}} S > 0$; efficiency: 4%; Carnot efficiency: 73%.

Photosystem II



Two photons split one water molecule, bring the electrons to plastocyanines, and pull four protons over the membrane. Eventually the protons are used to drive ATPase, and the electrons end up on NADPH. ATP and NADPH are then used in the dark reactions to make sugar.

Photosystem II, II

Thermodynamics
❖ Jennings
❖ Life
❖ Heat Machines
❖ pV diagram
❖ Conclusions
❖ Engines
❖ Efficiency
❖ Conclusions
❖ Bacteria
❖ Photosynthesis
❖ Work
❖ PSII
❖ ~~Jennings~~
❖ Second Law

Exercises and Problems

Work for splitting water and bringing the electrons to plastocyanine (Pc):

$$\frac{1}{2}\mathrm{O}_2 + 2\mathrm{H}^+ + 2\mathrm{e} \longrightarrow \mathrm{H}_2\mathrm{O} \quad \mathcal{E}^\ominus = 1.23\,\mathrm{V} \tag{6}$$

$$\mathrm{Pc}^{2+} + \mathrm{e} \longrightarrow \mathrm{Pc}^{+} \quad \mathcal{E}^\ominus = 0.372\,\mathrm{V} \tag{7}$$

Since there are two electrons involved in the process, the amount of work that needs to be performed to get the electrons from water to Pc is equal to

$$w = \Delta G^\ominus = 2 \times \mathrm{e} \times 0.86 = 2.75 \times 10^{-19}\,\mathrm{J} \tag{8}$$

Two 680 nm photons are needed to do this.

Photosystem II, III

- Heat taken from T_h:

$$2\frac{hc}{\lambda} = 5.84 \times 10^{-19}\,\mathrm{J} \tag{9}$$

- Entropy loss in the high temperature reservoir:

$$\Delta_h S = \frac{5.84 \times 10^{-19}}{1100} = 5.31 \times 10^{-22}\,\mathrm{J/K} \tag{10}$$

Photosystem II, IV

- Entropy gain in the low temperature compartment:

$$\begin{aligned}\Delta_l S &= \frac{5.84 \times 10^{-19} - 2.75 \times 10^{-19} - 4 \times 9.47 \times 10^{-21}}{300} \\ &= 9.03 \times 10^{-22}\,\mathrm{J/K} \qquad (11)\end{aligned}$$

Total change of entropy: $\Delta_{\mathrm{tot}} S > 0$; efficiency: 53%; Carnot efficiency: 73%.

Can Jennings be Correct?

NO

Living systems are pretty smart, but have not yet found a way to circumvent the second law of thermodynamics.

Auxiliary argument: if it were possible, everybody would be doing it.

The Second Law of Thermodynamics

- Clausius: Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.
- Kelvin: It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.
- Planck: The internal energy of a closed system is increased by an isochoric adiabatic process.
- Carathéodory: In every neighborhood of any state S of an adiabatically isolated system there are states inaccessible from S.

Does the second law have limitations?

Exercises and Problems

Exercises and Problems

Feynman’s solving problems algorithm according to Murray Gell–Mann:

1. write down the problem;
2. think very hard;
3. write down the answer.

Exercises and Problems

1. Carefully study the picture on slide 6. Did Carnot make an error?
2. Make sure that you understand, and if necessary derive, all expressions (1)–(10).
3. Look up the traditional textbook derivation of Carnot's efficiency. In other words: calculate heat and work for all parts of the ideal gas cycle in the figure on slide 11.
4. Do you think cytochromebc_1 always existed in bacterial photosynthesis? Why don't we find bacteria without it anymore?
5. Why does Duysens think light has a temperature of 1100 K, and not the temperature of sunlight (~ 6000 K).
6. Why is ΔG equal to the work performed in moving electrons? And how is ΔG related to the standard redox potentials?
7. Where do Jennings *et al.* make mistakes? (Tough problem, I am not sure if I know the answer, maybe it's in the literature already, see the paper by Knox and Parson.)
8. Find at least five papers in the last ten years in which it is claimed the second law can be, or is, violated.

Exercises and Problems

8. Read ref. 4. Comment on the number of photons they assume, and knowing what we know now, give a new estimate of the photosynthetic efficiency. Note that they use sugar as the final, stable, compound.
9. Use a quantum system (for instance a spin 1/2 in a magnetic field, or the quantum particle in a box) to derive the Carnot efficiency. Start by deriving isotherms and adiabats for such a system.
10. Many textbooks claim that all cycli between two temperatures have the same efficiency. In fact Atkins even goes so far as to claim: *All reversible engines have the same efficiency regardless of their construction* (6th Ed, p. 103). Show that this is not true (take some other cycle, for instance that of a Diesel or Stirling motor), and that in fact the Carnot cycle is the only cycle with the Carnot efficiency.
11. Argue that taking photons from a reservoir is the same as taking heat from it.

Literature

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4. W.E. Brittin and G. Gamov, Negative entropy and photosynthesis, *Proc. Natl. Acad. Sci. USA*, **47**, (1961), 724–727.
5. D.P. Sheehan, The Second Law of Thermodynamics: Foundations and Status, *Found. Phys.*, **37**, (2007), 1653–1658.
6. J. Uffink, Bluff Your Way in the Second Law of Thermodynamics, *Stud. Hist. Phil. Mod. Phys.*, **32**, (2001), 305–394.
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