

Module 5

Thermal Physics and Thermodynamics



UNIVERSITY OF COPENHAGEN



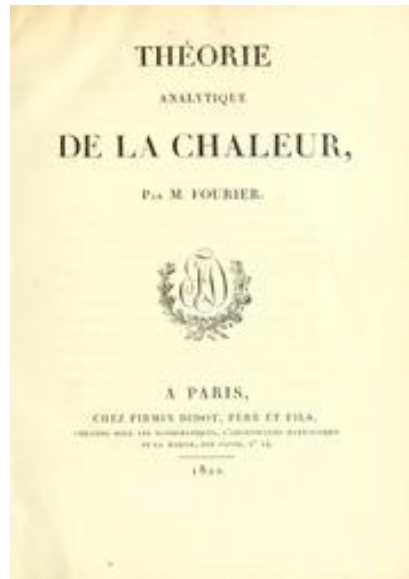
Introduction

- Extension vs. Depth dilemma
- Inventing temperature (Chang)
- Caloricum (Black) vs. Motion (Rumford)
- The tragicomical history of thermodynamics (Truesdell)
- Overview: Sources in Absalon
- Fourier's Theory of Heat Conduction
- Carnot's and Clausius's analysis of heat engines
- Kinetic gas theory (D. Bernoulli to Clausius)
- Statistical formulation (Maxwell, Boltzmann and Gibbs)

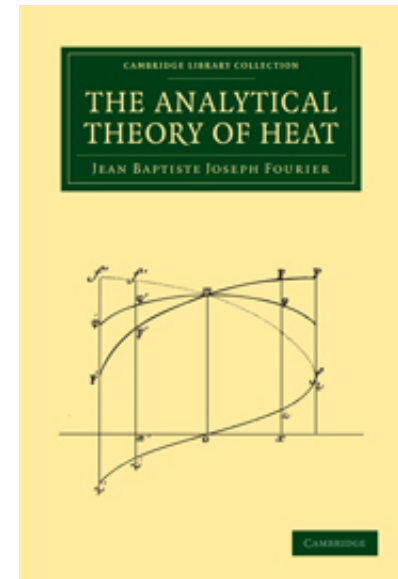
The Analytical Theory of Heat



Fourier (1768-1830)



(1807-1822)

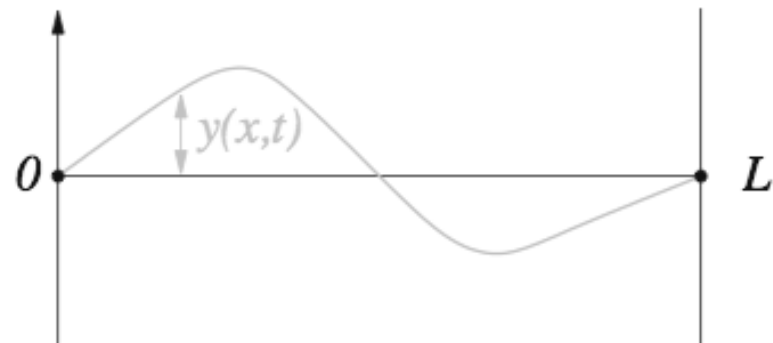
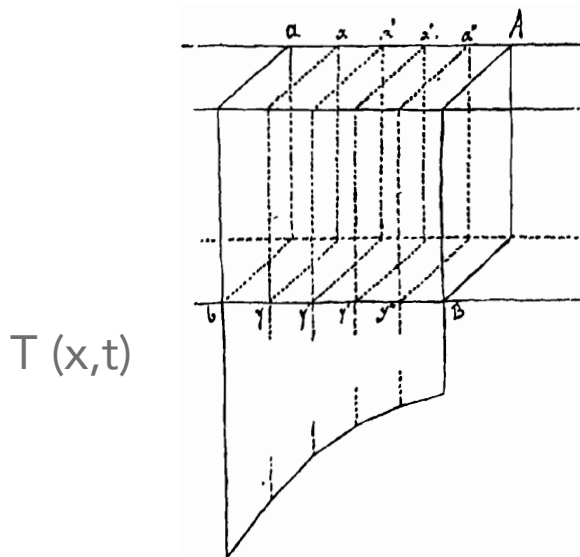


Alexander Freeman (1878)

Appraisal: Fourier's Theorie analytique de la chaleur is the bible of the mathematical physicist (Sommerfeld, 1947)

Problem statement

The problem of the propagation of heat consists in determining **what is the temperature at each point of a body at a given instant**, supposing that the initial temperatures are known (p. 14-15)

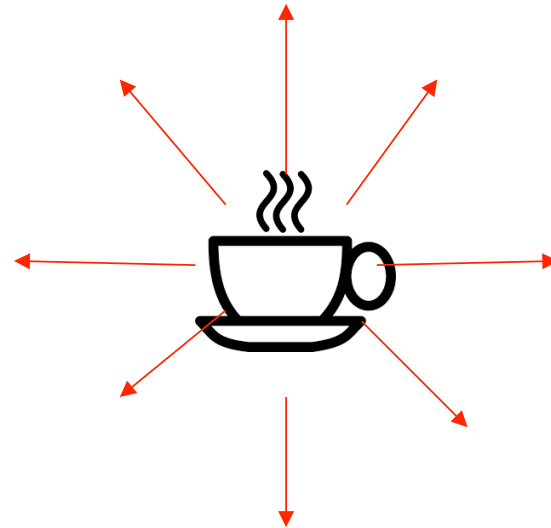
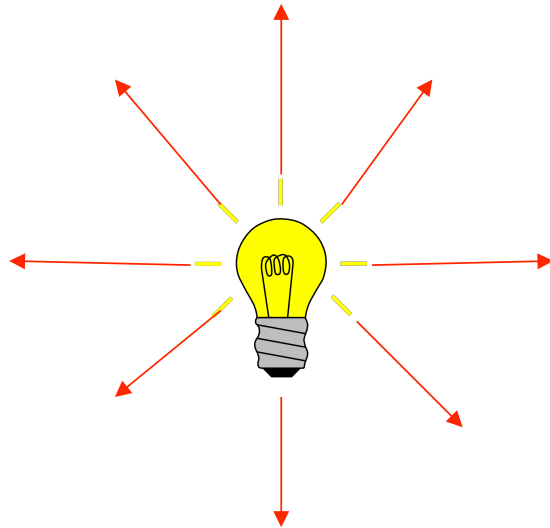


What is heat?

Primary causes are unknown to us (p. 1)

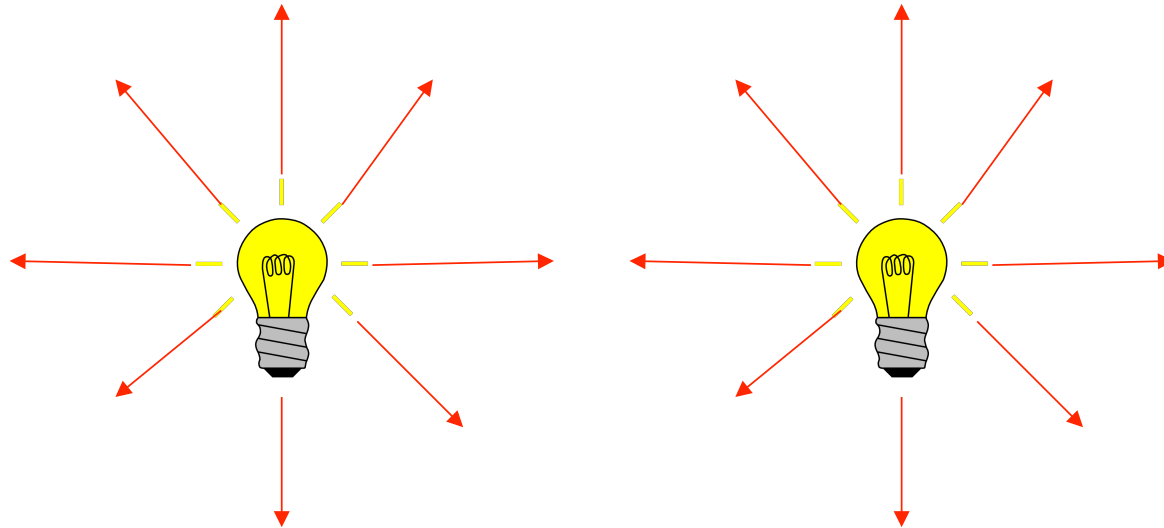
Of the nature of heat **uncertain hypotheses** only could be formed, but the **knowledge of the mathematical laws to which its effects are subject is independent of all hypotheses**; it requires only an attentive examination of the chief facts which common observations have indicated, and which have been **confirmed by exact experiments** (p. 26).

Physical assumptions – Heat and Light



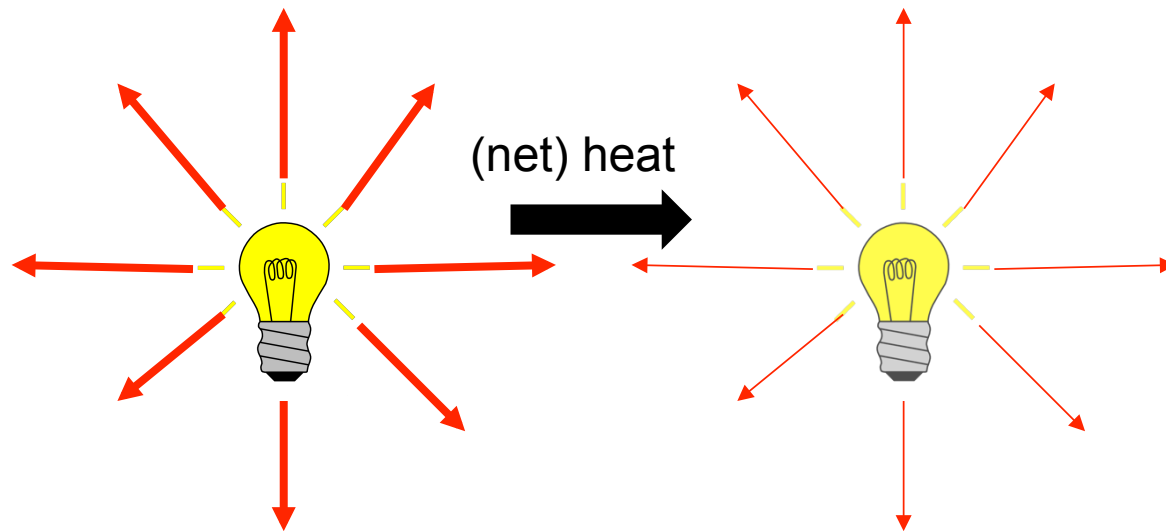
Of all modes of presenting to ourselves the action of heat, that which seems simplest and most conformable to observation, consists in **comparing this action to that of light**. Molecules separated from one another reciprocally communicate, across empty space, their **rays of heat**, just as shining bodies transmit their light (p. 32).

Physical assumptions – Heat conduction



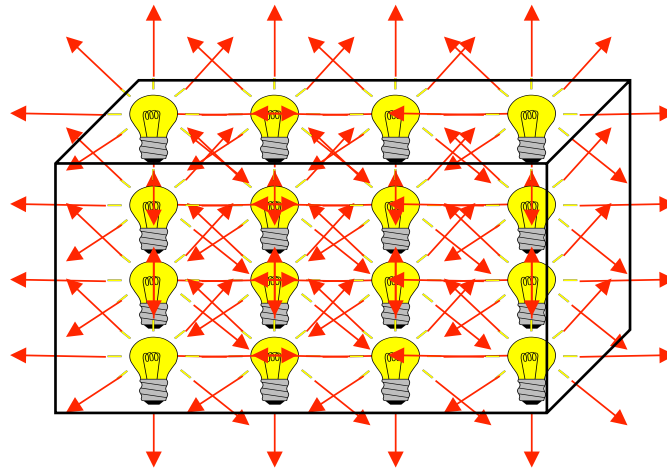
If two equal molecules are formed of the same substance and have the same temperature, each of them receives from the other as much heat as it gives up to it; their mutual action may then be regarded as null, since the result of this action can bring about no change in the state of the molecules (p. 41).

Physical assumptions – Heat conduction



If, on the contrary, the first is hotter than the second, it sends to it more heat than it receives from it; the result of the mutual action is the difference of these two quantities of heat. In all cases **we make abstraction** of the two equal quantities of heat which any two material points reciprocally give up; we conceive that the point most heated acts only on the other, and that, in virtue of this action, **the first loses a certain quantity of heat which is acquired by the second** (p. 41).

Physical assumptions – Interior and Exterior



In an opaque solid there is a very thin layer which is able to send its rays to exterior space. At a slightly deeper depth most of the heat projected toward the exterior is intercepted by the intermediate molecules (p. 34).

Definitions and Conventions

Temperature of melting ice $T = 0$

Temperature of boiling water $T = 1$

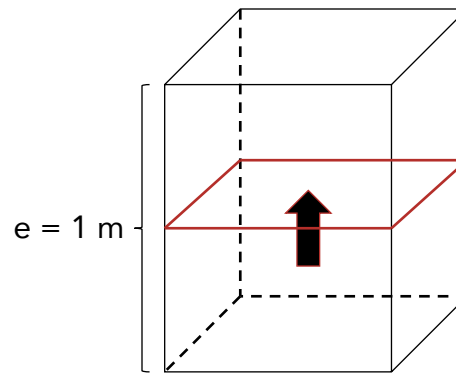
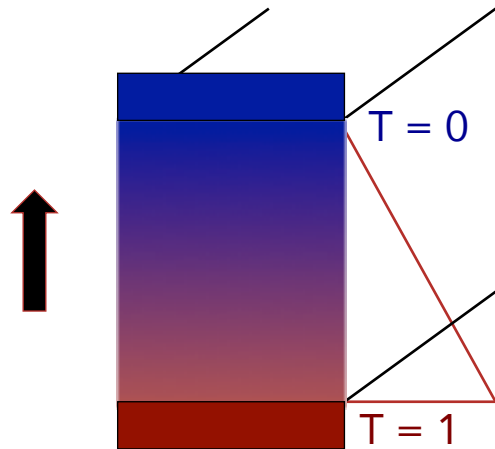
Unit of heat: Melt 1 kg of ice

Temperatures are proportional to the heat added

Three basic qualities (material dependent & determined experimentally)

K – Interior / Proper Conductivity

Facility with which heat is propagated in passing from one internal molecule to another



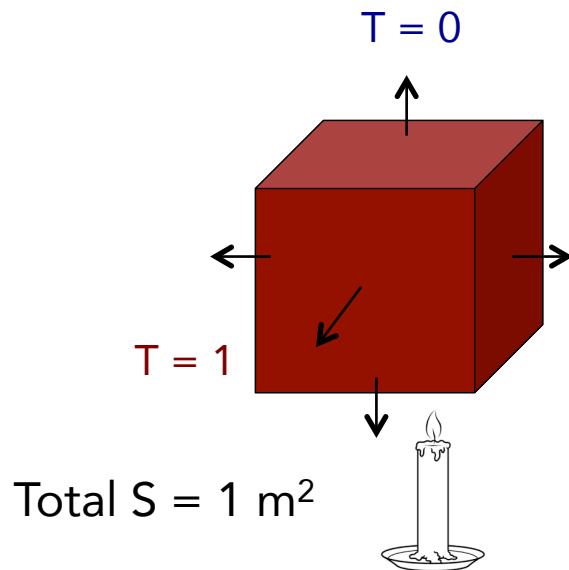
K is the quantity of heat that flows through 1 m² in 1 min

$$heat = -K \cdot S \cdot \frac{dT}{dx} \cdot dt$$

Three basic qualities (material dependent & determined experimentally)

h – External Conductivity / Penetrability

Facility with which the body's surface transmits heat to the atmospheric air



h is the quantity of heat that flows out of 1 m^2 to the air in 1 min

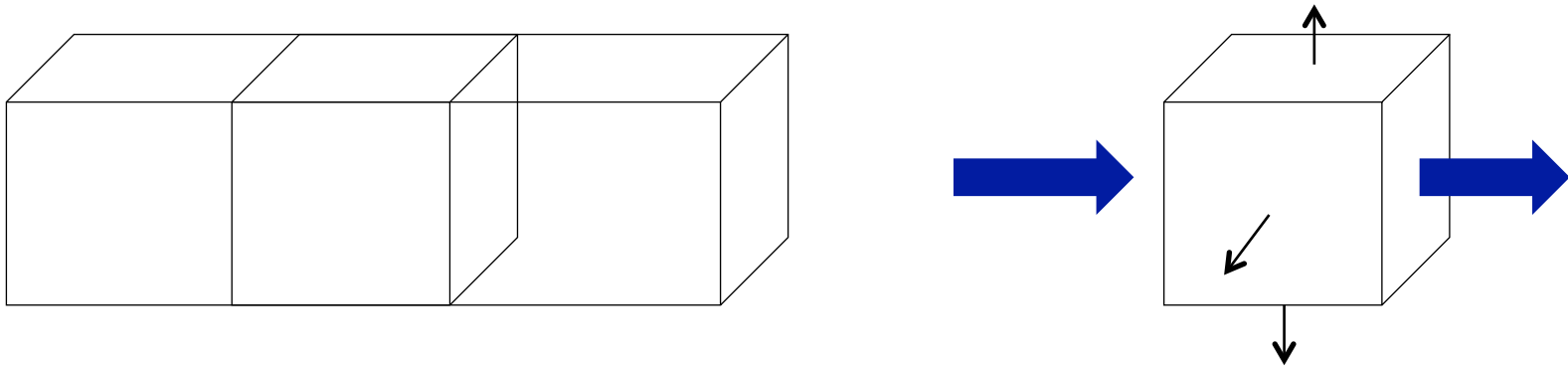
$$\text{heat} = h \cdot S \cdot T \cdot dt$$

Three basic qualities (material dependent & determined experimentally)

C – Specific capacity of heat

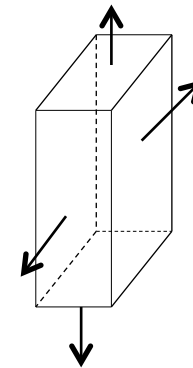
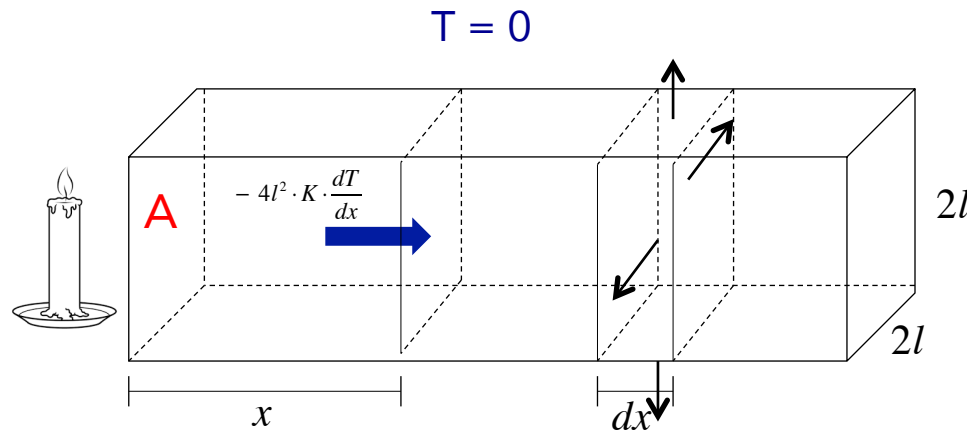
Quantity of heat that must be added to raise the temperature of 1 kg of the material from 0 to 1

$$\text{heat} = C \cdot D \cdot V \cdot dT$$



$$(\text{net heat gain}) = (\text{net internal heat flow}) - (\text{external heat flow}) = C \cdot D \cdot V \cdot dT$$

Permanent temperatures – Prism small thickness



heat out per unit time

$h \cdot T \cdot 8 \cdot l \cdot dx$ lamina

$\int_0^\infty h \cdot T \cdot 8 \cdot l \cdot dx = C$ prism

$C - \int_0^x h \cdot T \cdot 8 \cdot l \cdot dx$ right of section

Condition for permanent system of temperatures:

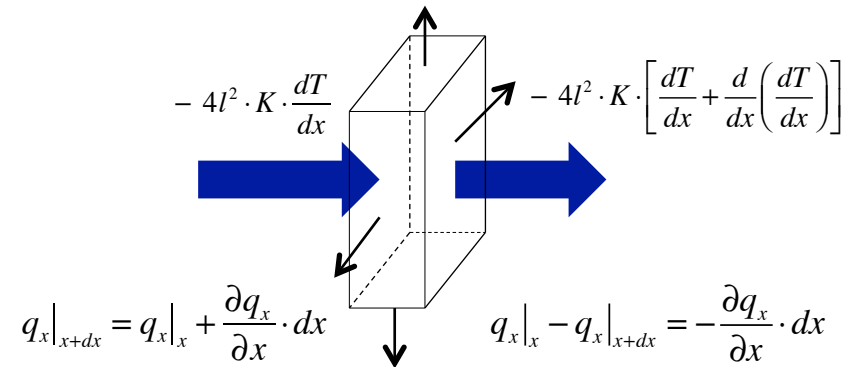
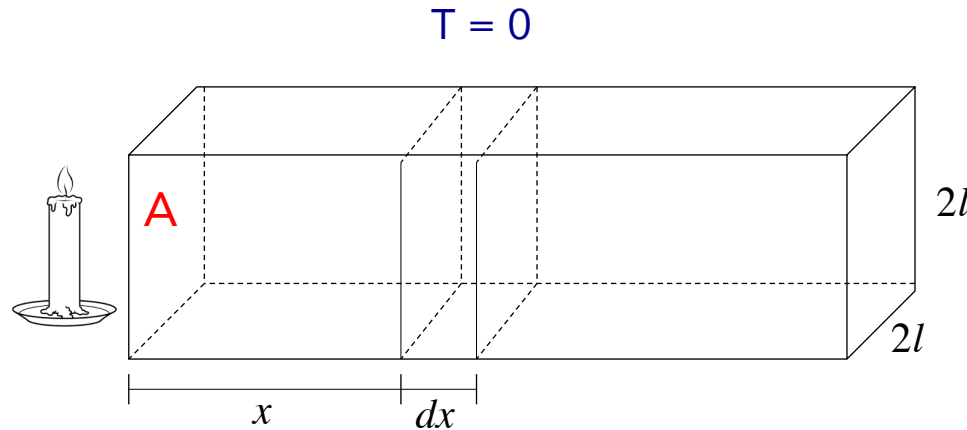
Quantity of heat that crosses a section (position x) per unit time **balances** all the heat that escapes through the external surface on the right of the section.

$$-4l^2 \cdot K \cdot \frac{dT}{dx} = C - \int_0^x h \cdot T \cdot 8 \cdot l \cdot dx$$

$$\frac{d^2T}{dx^2} = \frac{2 \cdot h \cdot T}{K \cdot l}$$



Permanent temperatures – Prism small thickness



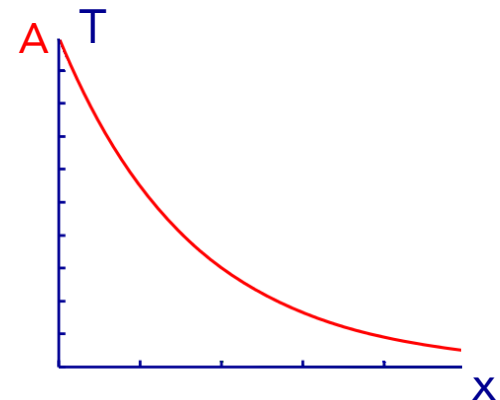
Condition for permanent system of temperatures: $q_x|_x - q_{x+dx} = 4l^2 \cdot K \cdot \frac{d^2T}{dx^2} \cdot dx$

Total amount of heat flow (per unit time) through the lamina is zero.

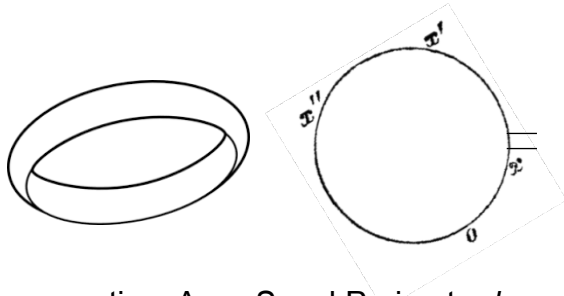
$$4l^2 \cdot K \cdot \frac{d^2T}{dx^2} \cdot dx = 8 \cdot h \cdot l \cdot T \cdot dx$$

$$\frac{d^2T}{dx^2} = \frac{2 \cdot h}{K \cdot l} \cdot T$$

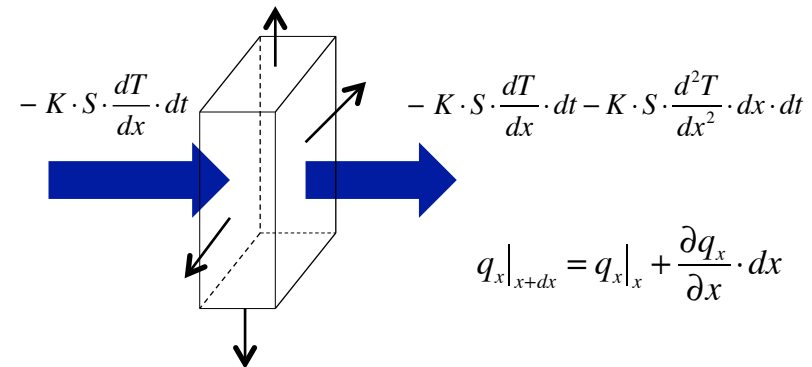
$$T(x) = A \cdot e^{-x \sqrt{\frac{2h}{Kl}}}$$



Movement of heat in a ring



Cross section: Area S and Perimeter l

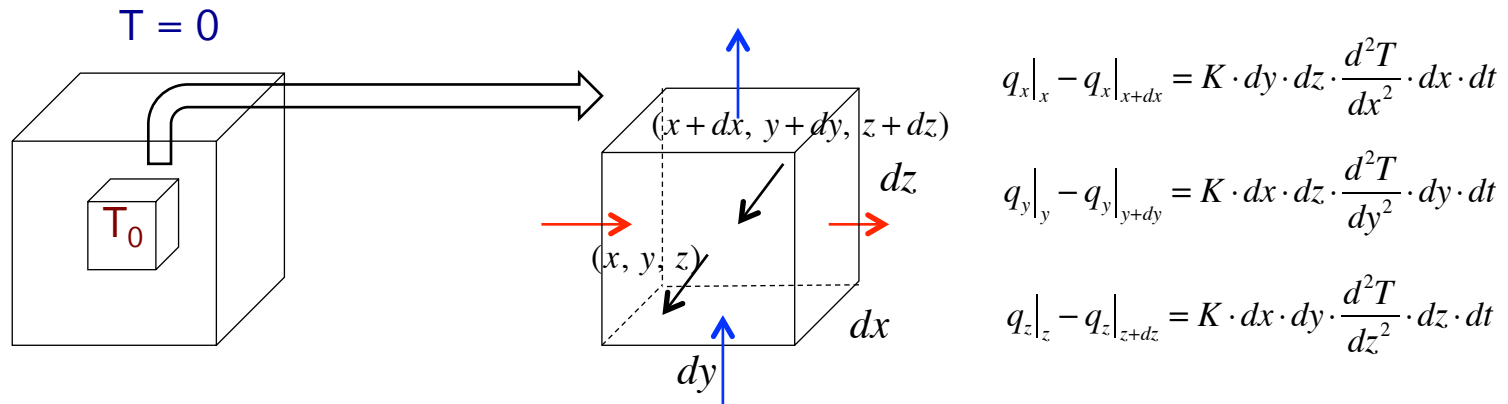


$$(\text{net heat gain}) = (\text{net internal heat}) - (\text{external heat})$$

$$C \cdot D \cdot V \cdot dT = K \cdot S \cdot \frac{d^2 T}{dx^2} \cdot dx \cdot dt - h \cdot T \cdot l \cdot dx \cdot dt$$

$$\frac{dT}{dt} = \frac{K}{CD} \cdot \frac{d^2 T}{dx^2} - \frac{hl}{CDS} \cdot T$$

Cube – Successive states of cooling



(net heat gain) = (net internal heat)

$$C \cdot D \cdot V \cdot dT = K \cdot dx \cdot dy \cdot dz \frac{d^2T}{dx^2} \cdot dt + K \cdot dx \cdot dy \cdot dz \frac{d^2T}{dy^2} \cdot dt + K \cdot dx \cdot dy \cdot dz \cdot \frac{d^2T}{dz^2} \cdot dt$$

$$\frac{dT}{dt} = \frac{K}{CD} \cdot \left(\frac{d^2T}{dx^2} + \frac{d^2T}{dy^2} + \frac{d^2T}{dz^2} \right)$$

Cube – Successive states of cooling (Heat Equation)

The equation arrived at in the preceding problem represents the movement of heat in the interior of all solids. Whatever, in fact, the form of the body may be, it is evident that, by decomposing it into prismatic molecules, we shall obtain this result (p. 104).

$$\frac{\partial T}{\partial t} = \alpha \cdot \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right)$$

The differential equations of the propagation of heat express the most general conditions, and **reduce the physical questions to problems of pure analysis**, and this is the proper object of theory (p. 6).

Some Lessons from the ATH

- Heat is a “means” notion for studying temperature distributions
- Non-dynamical framework (repulsive/expansive principles) “not produced by mechanical forces” (p. 23)
- “The effects of heat are subject to constant laws which cannot be discovered without the aid of mathematical analysis” (p. 14)
- From concrete examples to generalizations: “the consideration of simple and primary problems is one of the surest modes of discovering the laws of natural phenomena” (p. 132)
- Chapter II Section IX: Dimensional coherence $[L]^a \cdot [t]^b \cdot [T]^c$
- Fourier Analysis - “we may develop in convergent series, or express by definite integrals, functions which are not subject to a constant law, and which represent the ordinates of irregular or discontinuous lines” (p.22)

Some Lessons from the ATH

Quantity or Constant.	Length.	Duration.	Temperature.
Exponent of dimension of x ...	1	0	0
„ „ t ...	0	1	0
„ „ v ...	0	0	1
The specific conducibility, K ...	-1	-1	-1
The surface conducibility, h ...	-2	-1	-1
The capacity for heat, c ...	-3	0	1

- Chapter II Section IX: Dimensional coherence $[L]^a.[t]^b.[T]^c$
- Fourier Analysis - “we may develop in convergent series, or express by definite integrals, functions which are not subject to a constant law, and which represent the ordinates of irregular or discontinuous lines” (p.22)

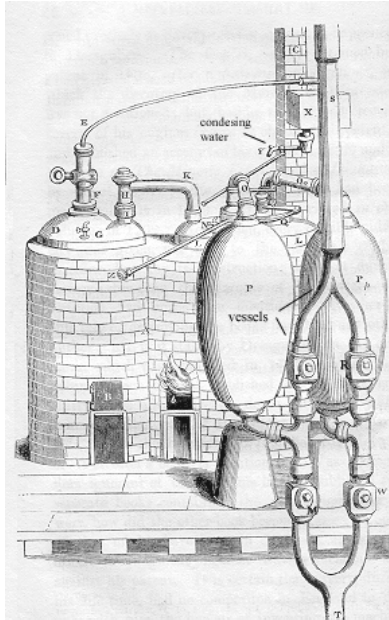
Some Lessons from the ATH



Jean Fourier
(1768-1830)

[...] mathematical analysis is as extensive as nature itself; it defines all perceptible relations, measures times, spaces, forces, temperatures; [...] It brings together phenomena the most diverse, and discovers the hidden analogies which unite them [...] it seems to be a faculty of the human mind destined to supplement the shortness of life and the imperfection of the senses (pp. 7-8).

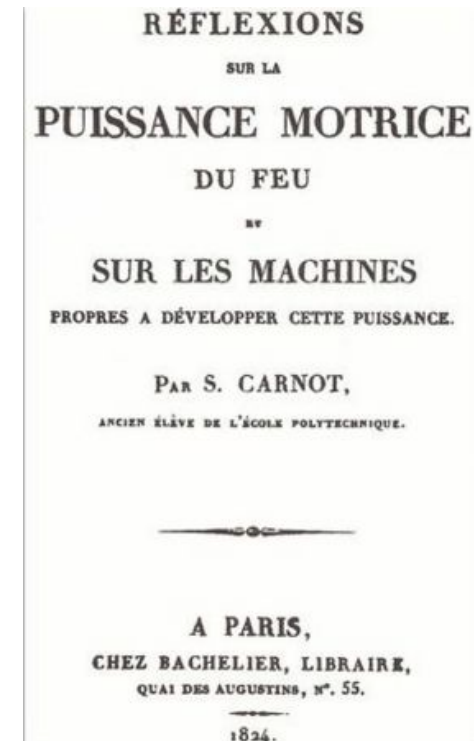
Reflections on the Motive Power of Fire



The Miner's Friend
Savery Engine (1698)



Nicolas L. Sadi
Carnot (1796-1832)



- Appraisal: "The **most original work ever written** in the physical sciences" (Schachtman); "The **founding work** of thermodynamics" (Thurston)
- Ignored for ten years (Clapeyron); Essential for Clausius and Kelvin

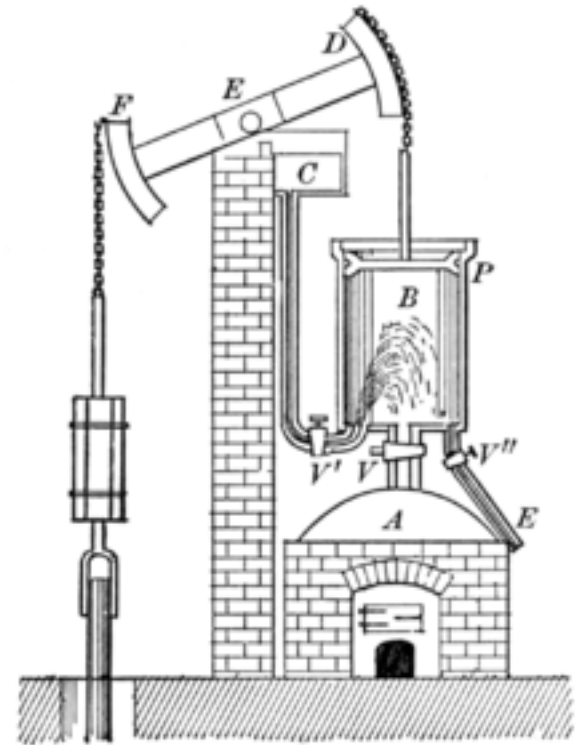
Reflections on the Motive Power of Fire

Introduction

EVERY one knows that **heat can produce motion**. That it possesses vast motive-power no one can doubt, in these days when the steam-engine is everywhere so well known.

[...]

The study of these engines is of the greatest interest, their importance is enormous, their use is continually increasing, and they seem destined to produce a **great revolution in the civilized world**.



Newcomen Engine (1712)

Reflections on the Motive Power of Fire

Maximum efficiency (Reversible engine, 223-224)

Direct

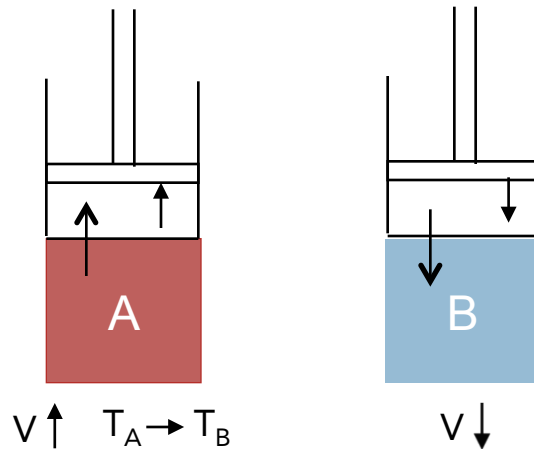
Reverse

Production of motive power

Consumption of motive power

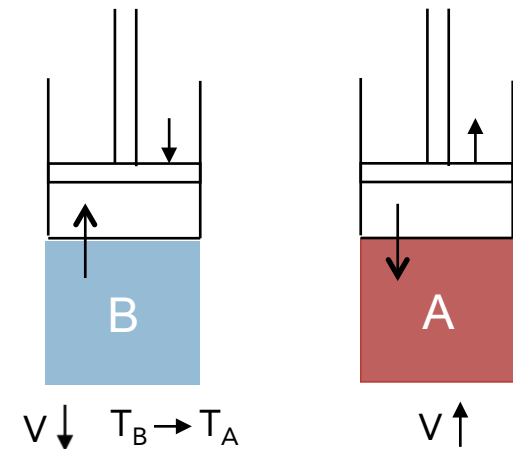
Caloric from A to B

Caloric from B to A



In both **same**
quantity of:

- Vapor
- Caloric
- Motive power



Now if it were possible to make the caloric produce a greater quantity of motive then in the engine described, it would suffice to divert a portion of this power to make the caloric of the body B return to the body A, to restore the initial conditions, and thus to be ready to commence again an operation precisely similar to the former, and so on: this would happen **without consumption** either of caloric or of any other agent whatever.

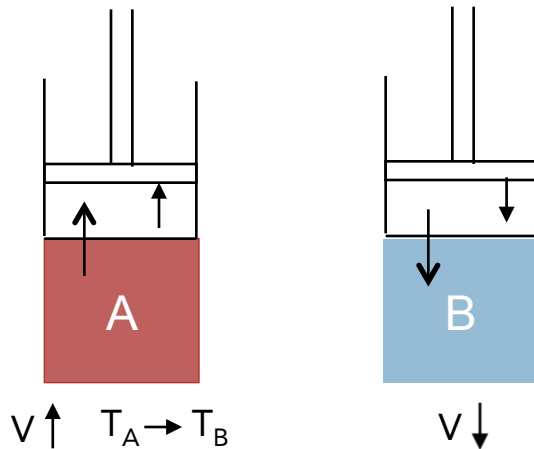
Reflections on the Motive Power of Fire

Maximum efficiency (Reversible engine, 223-224)

Direct

Production of motive power

Caloric from A to B



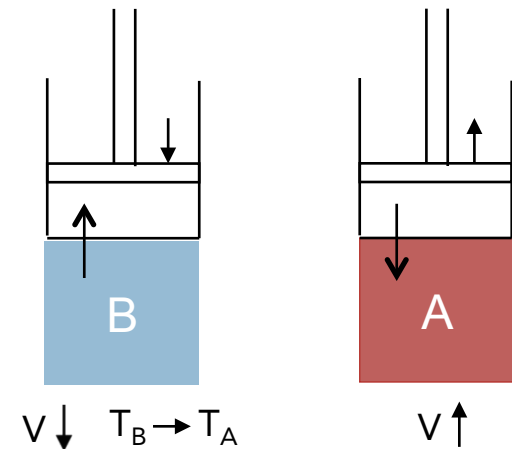
In both **same**
quantity of:

- Vapor
- Caloric
- Motive power

Reverse

Consumption of motive power

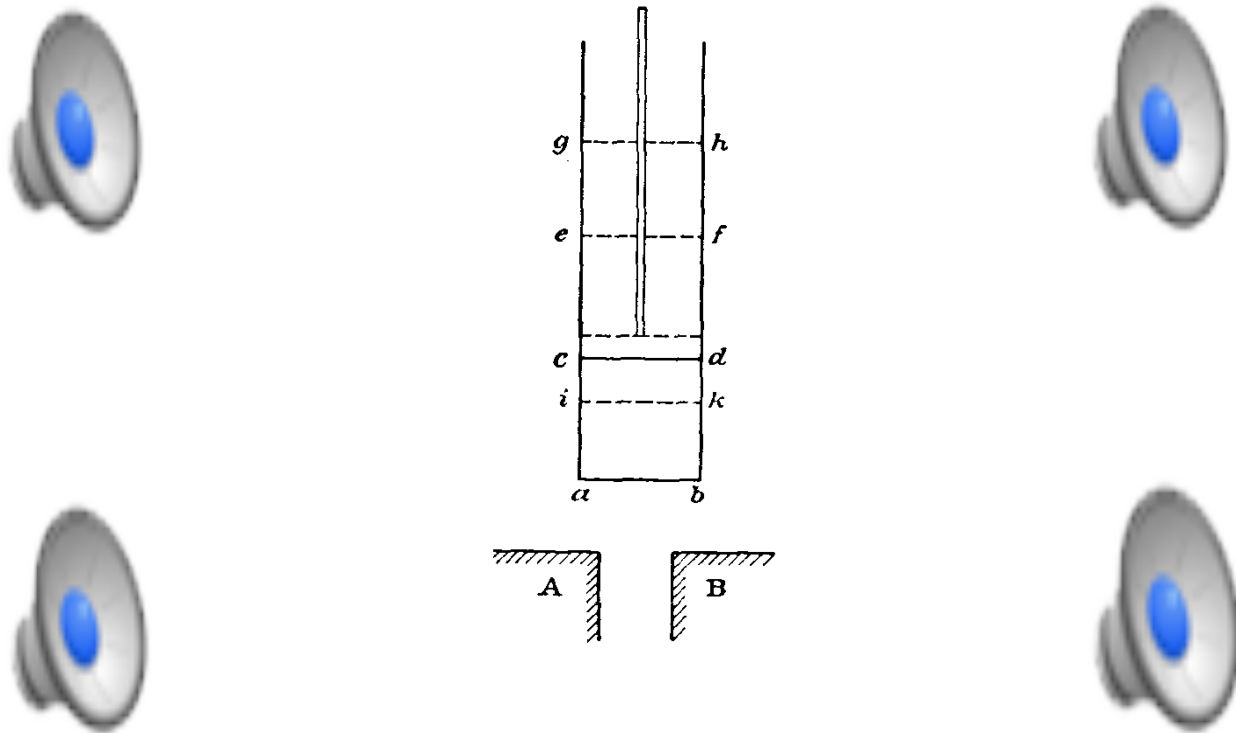
Caloric from B to A



Such a creation is entirely **contrary to ideas now accepted**, to the laws of mechanics and of sound physics. **It is inadmissible**. We should then conclude that the maximum of motive power resulting from the employment of steam is also the maximum of motive power realizable by any means whatever. *QED reductio ad absurdum*

Reflections on the Motive Power of Fire

Carnot Cycle (No ΔT which is not [only] due to ΔV)



Activity: Reverse engine (p. 227). Discuss/Draw in pairs

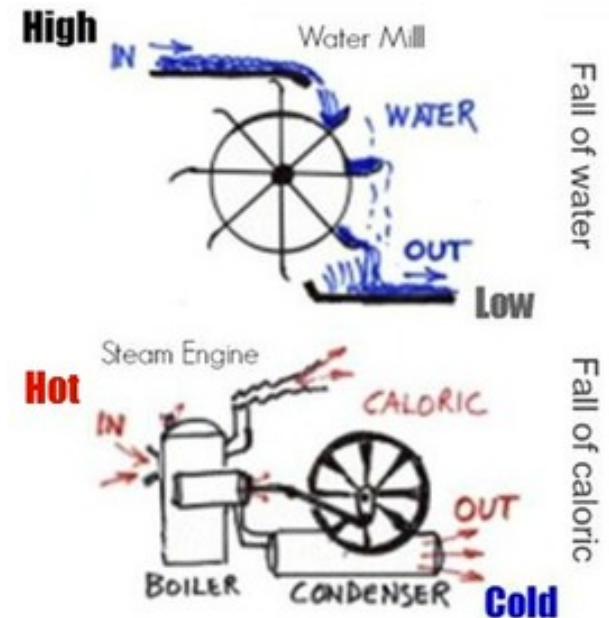
Reflections on the Motive Power of Fire

Main contributions

- Focus on cycles; Reversibility
- Motive power due to the “fall of caloric”, i.e., **independent of the material** of the working substance; depending **solely on the temperatures** between which the caloric is transported.

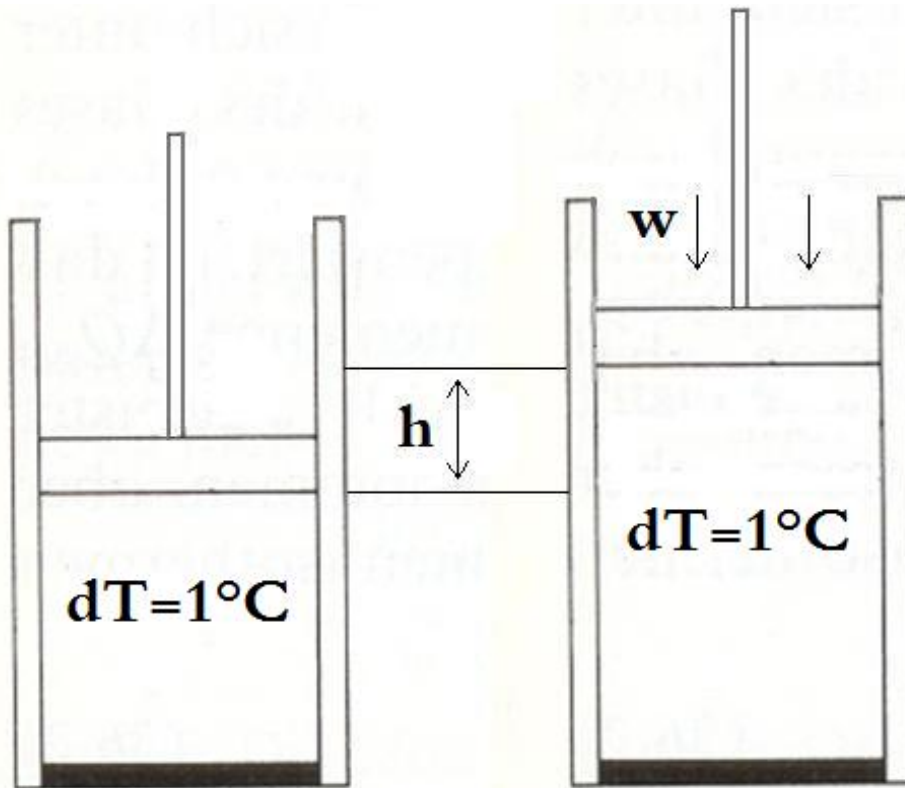
Some drawbacks

- Caloric (substance) is **conserved**
- Limited to **reversible** processes
- Confusion between caloric and heat



<http://www.eoht.info/>

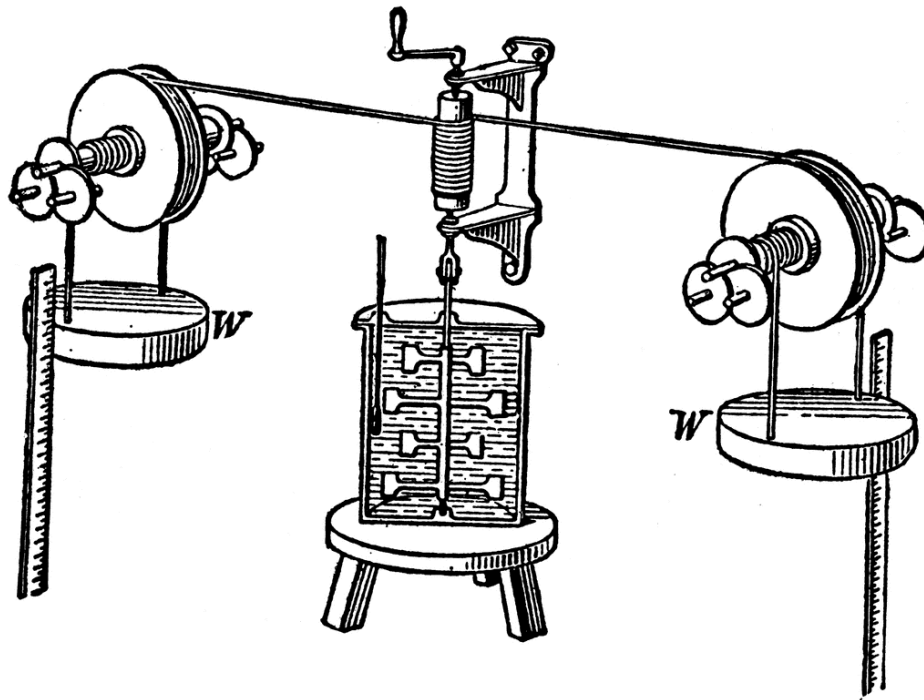
Mechanical equivalent of heat (Mayer, 1842)



α mech units = β thermal units

$$C_p - C_v = \text{Weight} \cdot \text{height}$$

Mechanical equivalent of heat (Joule, 1850)



α mech units = β thermal units

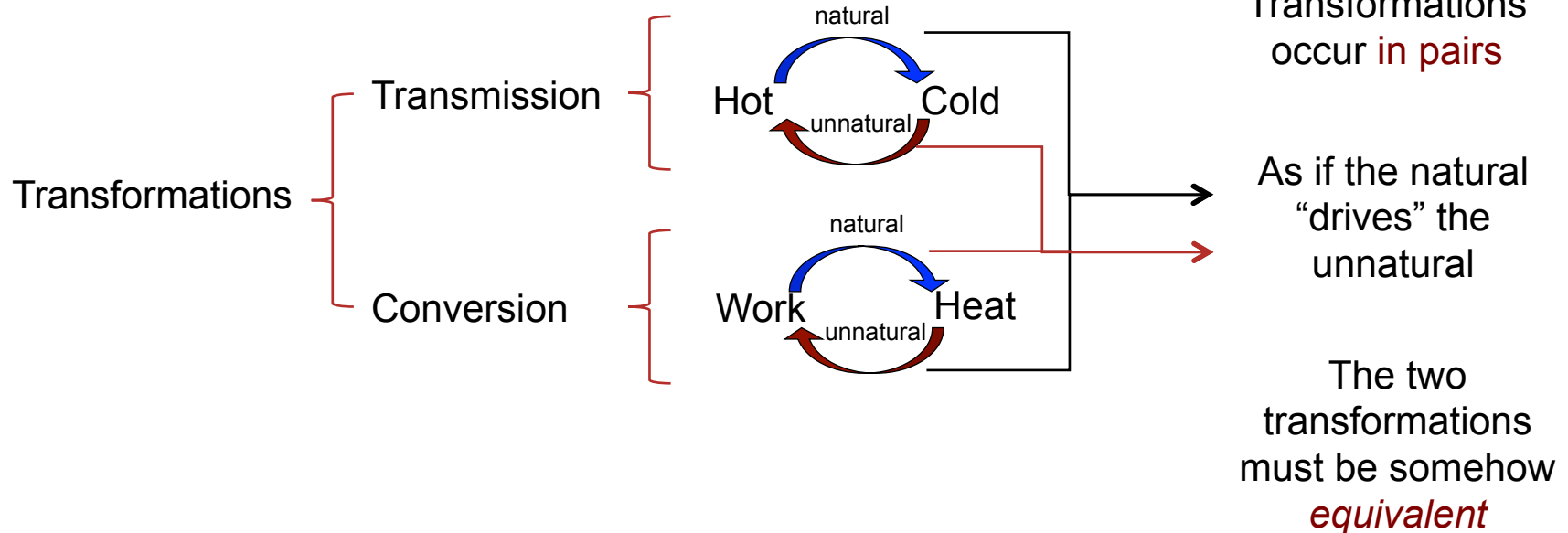
$$(W_1 - W_2) \cdot \text{height} = \text{Heat}$$

Clausius and the road to entropy

Rudolf Clausius (1854)

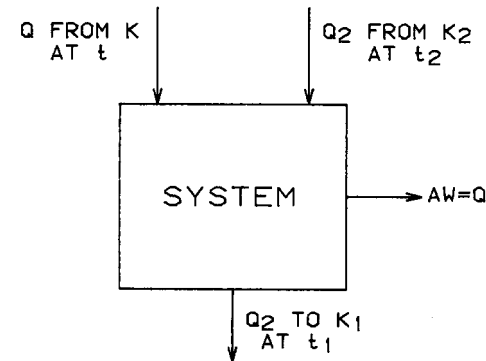
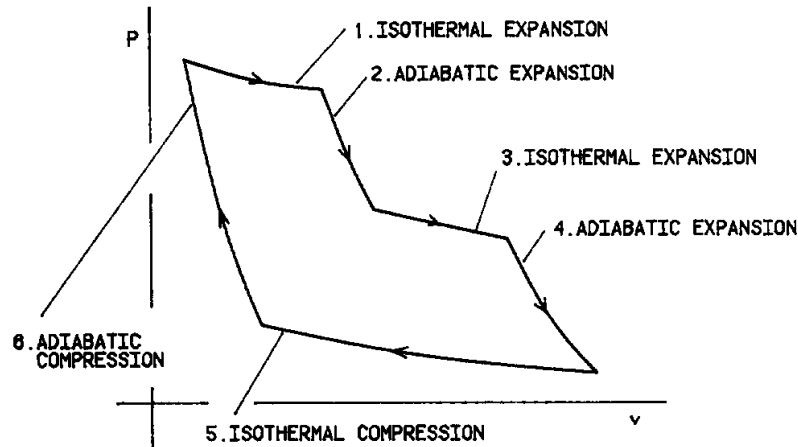
Appraisal: "This is one of the strangest memoirs in the entire history of physics" (Darrigol)

Conceptual framework



Rudolf Clausius (1854)

Clausius cycle



Transformations in
Clausius cycle

$$\left\{ \begin{array}{l} Q[t] \rightarrow W \\ Q_2[t_2] \rightarrow Q_2[t_1] \end{array} \right\}$$

Transformations in
Clausius cycle (reverse)

$$\left\{ \begin{array}{l} W \rightarrow Q[t] \\ Q_2[t_1] \rightarrow Q_2[t_2] \end{array} \right\}$$

Doctrine of specific
and latent heats

$$dQ = C_v(t, V) dt + \lambda(t, V) dV.$$

From Clausius (1850)

$$dQ = dU + APdv.$$

Meaning of dU

Mechanical energy (Kelvin 1)

Intrinsic energy (Kelvin 2)

Internal energy (Helmholtz)

$$\int dQ = \int dU + A \int Pdv$$

$$\int dQ = Q + Q_2 - Q_2 = Q \quad \int Pdv = W \quad \int dU = 0$$

$$Q = AW$$

Rudolf Clausius (1854)

Äquivalenzwert: The predecessor of Entropy

“Equivalent” transformations in Clausius cycle

$$\left\{ \begin{array}{l} Q[t] \rightarrow W \\ Q_2[t_2] \rightarrow Q_2[t_1] \end{array} \right\}$$

“Equivalent” transformations in Clausius (reverse) cycle

$$\left\{ \begin{array}{l} W \rightarrow Q[t] \\ Q_2[t_1] \rightarrow Q_2[t_2] \end{array} \right\}$$

We see, therefore, that these two transformations may be regarded as phenomena of the same nature, and we may call two transformations which can thus mutually replace one another *equivalent*. We have now to find the law according to which the transformations must be expressed as mathematical magnitudes, in order that the equivalence of two transformations may be evident from the equality of their values. The mathematical value of a transformation thus determined may be called its *equivalence-value* (Äquivalenzwerth).

Assumption: The equivalence value is proportional to the amount of heat transformed and to the temperature (or temperatures) involved

Convention: Natural +

$$\left. \begin{array}{l} \text{Equivalence value for the} \\ \text{conversion transformation} \\ W \rightarrow Q[t] \end{array} \right\} = f(t)Q,$$

$$\left. \begin{array}{l} \text{Equivalence value for the} \\ \text{transmission transformation} \\ Q_2[t_2] \rightarrow Q_2[t_1] \end{array} \right\} = F(t_2, t_1)Q_2$$

Unnatural –

$$\left. \begin{array}{l} \text{Equivalence value for the} \\ \text{conversion transformation} \\ Q[t] \rightarrow W \end{array} \right\} = -f(t)Q,$$

$$\left. \begin{array}{l} \text{Equivalence value for the} \\ \text{transmission transformation} \\ Q_2[t_1] \rightarrow Q_2[t_2] \end{array} \right\} = -F(t_2, t_1)Q_2$$

Rudolf Clausius (1854)

Properties of the equivalence values

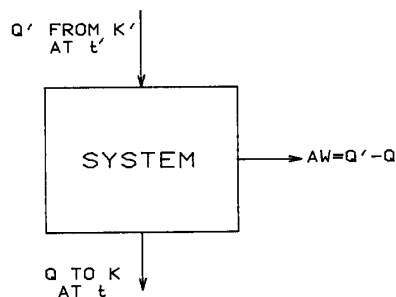
Clausius cycle

$$\left\{ \begin{array}{l} Q[t] \rightarrow W \\ Q_2[t_2] \rightarrow Q_2[t_1] \end{array} \right\} \quad F(t_2, t_1)Q_2 - f(t)Q = 0.$$

Another Clausius cycle

$$\left\{ \begin{array}{l} Q'[t'] \rightarrow W \\ Q_2[t_2] \rightarrow Q_2[t_1] \end{array} \right\} \quad F(t_2, t_1)Q_2 - f(t')Q' = 0$$

Yet another [Carnot] cycle



$$F(t', t)Q - f(t')(Q' - Q) = 0$$

Back to Clausius cycle

$$f(t_2)Q_2 - f(t_1)Q_2 + f(t)Q = 0$$

Back to Carnot cycle

$$f(t')Q' - f(t)Q = 0$$

Thus

$$f(t)Q = f(t')Q'$$

The magnitude of $f(t)$ is **inversely proportional** to the amount of heat transformed

Combined with $f(t)Q = f(t')Q'$ yields

$$F(t', t) = f(t) - f(t')$$

Meaning: Only **one** function ($f(t)$) is needed

Both equations of the form

$$\sum f(t)Q = 0$$

Rudolf Clausius (1854)

Properties of the equivalence values

it is evident that the passage of the quantity of heat Q , from the temperature t_1 to the temperature t_2 , has the same equivalence-value as a double transformation of the first kind, that is to say, the transformation of the quantity Q from heat at the temperature t_1 into work, and from work into heat at the temperature t_2 . A discussion of the question how far this external agreement is based upon the nature of the process itself would be out of place here*; but at all events, in the mathematical determination of the equivalence-value, every transmission of heat, no matter how effected, can be considered as such a combination of two opposite transformations of the first kind.

$$F(t', t) = f(t) - f(t') \quad \text{Meaning: Only one function } (f(t)) \text{ is needed}$$

Back to Clausius cycle

Back to Carnot cycle

Both equations of the form

$$f(t_2)Q_2 - f(t_1)Q_2 + f(t)Q = 0 \quad f(t')Q' - f(t)Q = 0$$

$$\sum f(t)Q = 0$$

Rudolf Clausius (1854)

Mathematical analogy

$$\sum f(t)Q = 0 \quad (\text{reversible, cyclic processes})$$

$$\int f(t)dQ = 0 \quad (\text{reversible, cyclic processes}) \quad \text{Infinite number of steps, each one involving an infinitesimal heat transfer of amount } dQ \text{ at a temperature } t$$

What is the form of function $f(t)$?

Because $\int f(t)dQ = 0$ it can be argued [mathematically] that $f(t)dQ$ is the differential of some (other) state function (e.g. C) depending on the state variables $C(v,t)$

$$dC = f(t)dQ$$

If dC is an exact differential

$$dC = \frac{\partial C}{\partial v} dv + \frac{\partial C}{\partial t} dt$$

Equality of crossed derivatives

$$\left[\frac{\partial}{\partial t} \left(\frac{\partial C}{\partial v} \right)_t \right]_v = \left[\frac{\partial}{\partial v} \left(\frac{\partial C}{\partial t} \right)_v \right]_t$$

$$\text{But } dQ = Mdv + Ndt \quad \text{thus} \quad dC = f(t)dQ = f(t)Mdv + f(t)Ndt$$

$$\left[\frac{\partial}{\partial t} \left(\frac{\partial C}{\partial v} \right)_t \right]_v = f'(t)M + f(t) \left(\frac{\partial M}{\partial t} \right)_v = \left[\frac{\partial}{\partial v} \left(\frac{\partial C}{\partial t} \right)_v \right]_t = f(t) \left(\frac{\partial N}{\partial v} \right)_t$$

Rudolf Clausius (1854)

Hang on, we are almost there!

From = crossed derivatives $f'(t)M = f(t) \left[\left(\frac{\partial N}{\partial v} \right)_t - \left(\frac{\partial M}{\partial t} \right)_v \right]$ thus $f'(t)M = -A f(t) \left(\frac{\partial P}{\partial t} \right)_v$

Previously Clausius shows that $\left[\left(\frac{\partial N}{\partial v} \right)_t - \left(\frac{\partial M}{\partial t} \right)_v \right] = -A (\partial P / \partial t)_v$

For Clausius $f(t)$ was a universal/unique function. So he considered the ideal gas...

$$Pv = R(a + t)$$

For an isothermal expansion

which leads to $\left(\frac{\partial P}{\partial t} \right)_v = R/v$

$$dQ = Mdv \quad dQ = APdv$$

All heat
converted
into work

Substituting $f'(t) = -f(t)/(a + t)$ Solving $f(t) = (\text{constant})/(a + t)$

Thus $dC = (\text{constant})dQ/(a + t)$ The constant's value is arbitrary (scale for C)

$dC = dQ/(a + t)$ thus $dC = dQ/T$

Rudolf Clausius (1854)

$$\int f(t) dQ = 0 \quad (\text{reversible, cyclic processes})$$

$$dC = f(t) dQ \quad dC = dQ / T$$

$$\int dQ / T = 0 \quad (\text{reversible, cyclic processes})$$

What about *non-reversible* cycles?

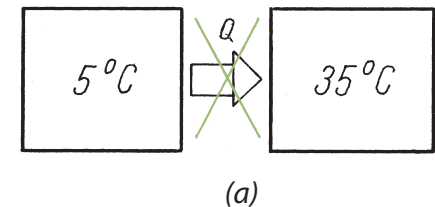
The algebraical sum of all transformations occurring in a cyclical process can only be positive.

A transformation which thus remains at the conclusion of a cyclical process without another opposite one, and which according to this theorem can only be positive, we shall, for brevity, call an *uncompensated* transformation.

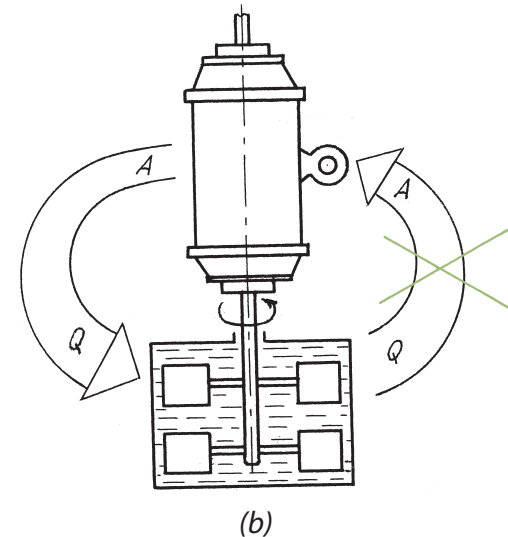
The different kinds of operations giving rise to uncompensated transformations are, as far as external appearances are concerned, rather numerous, even though they may not differ very essentially. One of the most frequently occurring examples is that of the transmission of heat by mere conduction, when two bodies of different temperatures are brought into immediate contact; other cases are the production of heat by friction, and by an electric current when overcoming the resistance due to imperfect conductivity, together with all cases where a force, in doing

Various formulations of the 2nd law

(a) Heat cannot of itself pass from one body to a hotter body without additional processes participating in the system. The possibility of other processes must be emphasized, because in a refrigeration system, a body can have heat extracted from it and passed to the warmer environment; however, there complex processes are involved.



(b) A quantity of heat cannot be transformed into mechanical work with 100% efficiency. The work done by the motor here is transformed completely into heat, but this heat cannot be completely turned back into work. Hence, the arrangement shown will not work, even though it does not contravene the law of conservation of energy.



Was Carnot wrong after all?

$$\int dQ/T = 0 \quad (\text{reversible, cyclic processes})$$

In fact, there **are two heat quantities** that it is useful to define. One is conserved in any reversible process, whether work is done or not—in modern terms, the **entropy**; the other is conserved by a body in adiabatic calorimetry—in modern terms, the quantity of heat or heat energy. Neither quantity is any more fundamental than the other. It is through a historical accident, an arbitrary choice, that we happen to call one of these quantities by the familiar term “heat” and the other by a pseudo-Greek name. In the early nineteenth century **the two were confused**. The writers of that time also had two names for the heat available, but when we read any paper of this period, “quantity of heat” and “quantity of caloric” must each be construed to mean sometimes “change of entropy” and sometimes “quantity of heat.” Carnot himself stated explicitly that he used the two terms interchangeably; in fact, **he had a tendency to reserve the term “caloric” for situations where we should now talk of entropy**. For example, he usually wrote that in a reversible heat-engine, the amounts of **caloric absorbed by the working substance at the high temperature and lost at the low were compensated** (Mendoza, 1960).

Is there a consensus among scientists today?

How physicists disagree on the meaning of entropy

Robert H. Swendsen^{a)}

Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

(Received 29 June 2010; accepted 30 November 2010)

Discussions of the foundations of statistical mechanics, how they lead to thermodynamics, and the appropriate definition of entropy have occasioned many disagreements. I believe that some or all of these disagreements arise from differing, but unstated assumptions, which can make opposing opinions difficult to reconcile. To make these assumptions explicit, I discuss the principles that have guided my own thinking about the foundations of statistical mechanics, the microscopic origins of thermodynamics, and the definition of entropy. The purpose of this paper will be fulfilled if it paves the way to a final consensus, whether or not that consensus agrees with my point of view. © 2011 American Association of Physics Teachers.

[DOI: 10.1119/1.3536633]

End of module feedback

- Please go to b.socrative.com (student login)
- Enter the HISPHYSKU room
- Fill out the short (anonymous) survey
- Tak skal du have!