Thermodynamics

is the science which deals with systems
(I.e. delimited portions of matter) which undergo
any form of energy exchange.

It arose form the studies on the first thermal machines
(steam engines etc.) at the beginning of XIX century.

Within few decades it was extended
to describe any form of process,
including chemical and then biological transformations.

At the half of XX century mathematicians observed
that thermodynamics is also able
to describe information exchanges,
so it is now the basis for information technology.

Thermodynamics was early derived
from empirical observations on objects,
and from very simple mathematical models
which described the transformations they undergo.

It is based upon four “Laws”,
any of which can be formulated in many ways,
in plain language or (more usually) in mathematical form.

The First and the Second Law were formulated
by several scientists more or less at the same time (1845 -1855).

After some decades the Third Law was introduced.

As in modern thermodynamics it is recognized that a fourth law
is necessary (although formerly given as implicit)
to justify the first two, it was given the name of Zeroeth Law

Here are the common enunciates of the four laws.
Although even in plain language they appear quite exoteric, what is worth in our discussions is just to understand that they have proven to be some of the most powerful tools to understand nature.

0 If three or more systems are in thermal contact with each other, and all in equilibrium together, then any two taken separately are in equilibrium with one another.

1 In any process, energy can be changed from one form to another, but it is never created or destroyed.

2

According to Rudolf Clausius:

"It is impossible for a self- acting machine, unaided by external agency, to convey heat from a body at one temperature to another body at a higher temperature."

According to William Thomson, Lord Kelvin:

“It is impossible by a cyclic process to take heat from a reservoir and convert it into work without, in the same operation, transferring heat from a hot to a cold reservoir.”

3 Entropy of a perfect crystal at 0 K is zero.

First and Second Law are often quoted by the famous Clausius' sentence:

Die Energie der Welt ist konstant.
Die Entropie der Welt strebt einem Maximum zu.

Internal Energy is defined as the funcion U,
such that for any transformation on a system:

$$\Delta U = Q - L$$

when Q is the heat exchanged and L is the work done.

Entropy has originaly been defined as the function S, such that

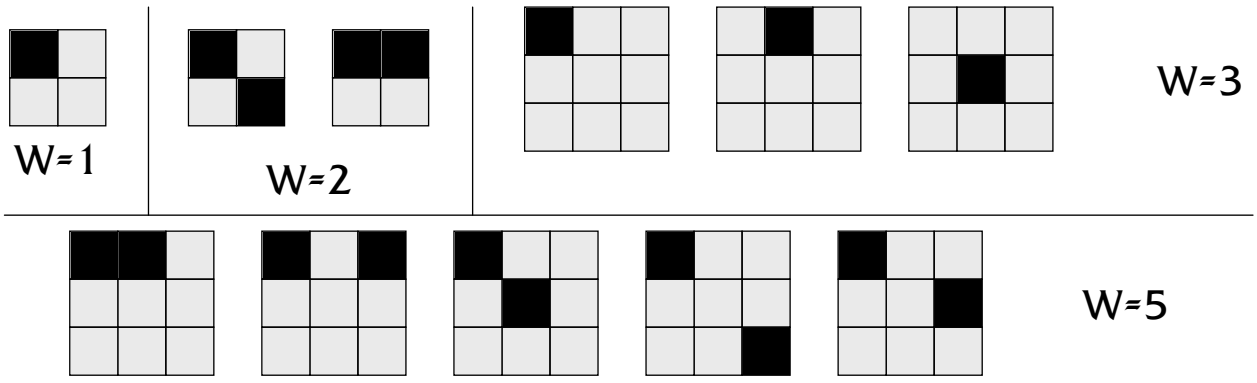
$$dS = \frac{dQ}{T}$$

if dQ is the heat which is exchanged in a microscopically reversible process, and T is the temperature.
This "Clausius' definition" derives from the study
of thermal machines and heat exchangers
after the works of Carnot, Joule, Hess, Kelvin etc.

A completely different equation, but perfectly equivalent to the former, is the following one, due to Boltzmann :

$$S_W = k \ln W$$

where the entropy of a system is defined in terms of the number of different states which a system can assume:



Entropy is then also a measure of *disorder.*
The number of atoms in any piece of matter which is visually detectable is in the order of *billions of billions.*

Reversibility: Dealing with A Ghost

Sergio Palazzi

1851: Ruskin's "The Stones of Venice"

1848: Kelvin, absolute thermometric scale

1845: Joule, internal energy

1840: Viollet-le-Duc at Carcassonne

1824: Carnot's *"Refléxions"*

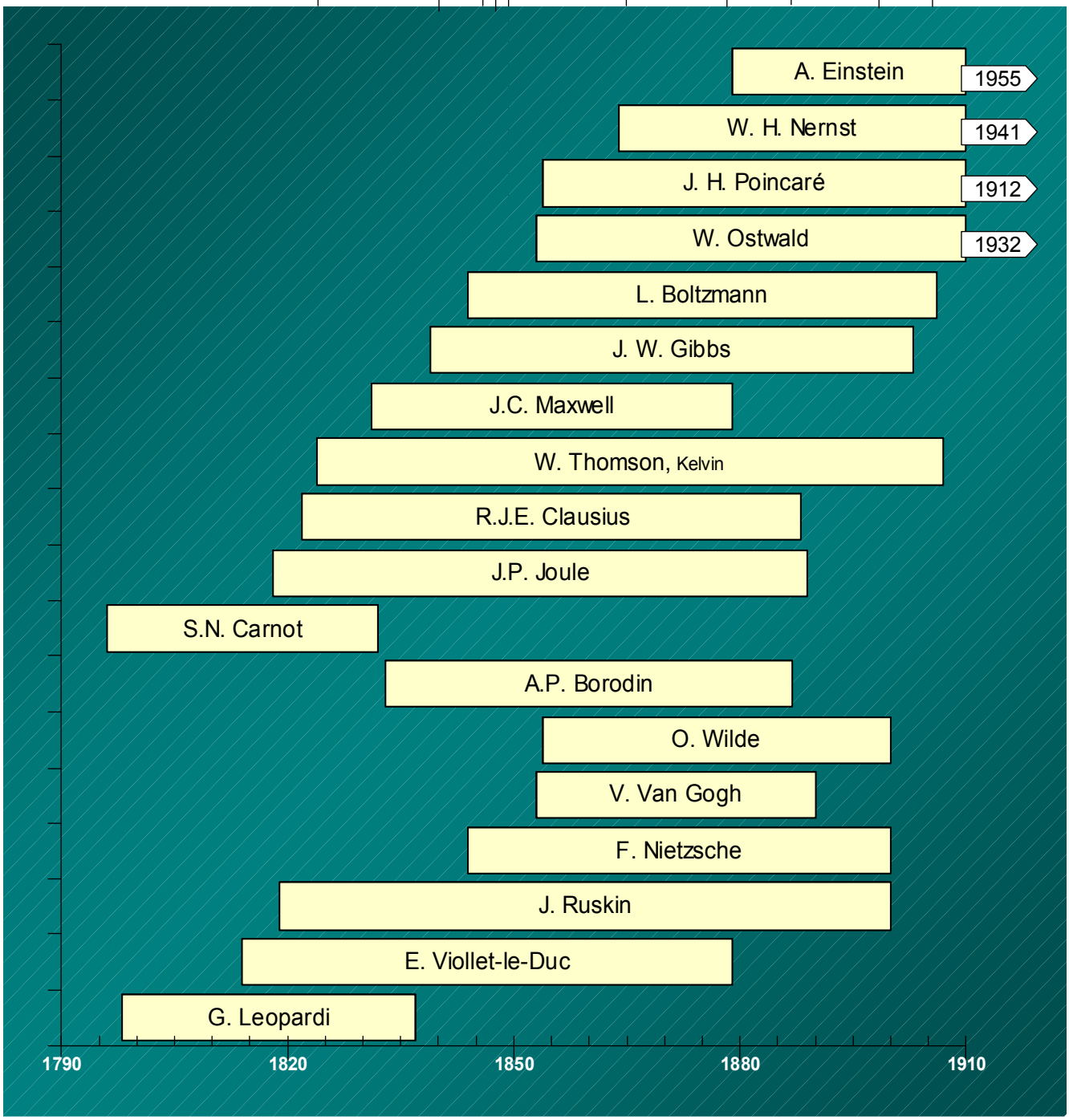
1865: Clausius: entropy

1878: Gibbs: free energy

1887: Ostwald's "Physical chemistry"

1898: St. Gall Conference

1906: Nernst: third law



When you can measure what you are speaking about
and express it in numbers
you know something *about it;*
but when you cannot measure it,
when you cannot express it in numbers
your knowledge is of a meagre
and unsatisfactory kind

Lord Kelvin, 1883

Since the beginning of culture,sciences and humanities
have been walking together,
speaking similar languages.
The Old Alliance seems to be broken
since XVIII century,
as Western science began to speak in numbers,
to quantify results, to search for objectivity.

This has meant an extraordinary acceleration
and great advantages for mankind.
But their results very often appeared too cold
and far from common experience and passions.

Artists and philosophers have largely
rejected the mathematical approach.
Both idealists and irrationalists are often
even *proud* to ignore quantitative sciences.

...with A Ghost?

...the personification of an idea
Of a desire
Of a fear
Of the consequences of evil...

...Mathematical models
Chemical formulæ
Physical theoretical experiments
Moral allegories...

we are rather used to dealing with ghosts;
some of them can be really useful
as we know that they are just in our minds.

Reversibility was already a ghost in natural sciences before this word was born in conservators' speech. However, its believers are making great efforts because of it.

It's true that being afraid of it can prevent us from mistakes, but it also encourages superstitious irrationality.

The starting point of the "reversibility principle"
in the science of conservation (XIX century):

avoiding *definitely irreversible mistakes*
caused by wrong or arbitrary treatments
(I.e.: radical cleaning, "as it was" reconstructions,
using of poorly experienced modern materials).

As early as 1898, the St. Gall Conference
on manuscript preservation
stated some empirical and flexible criteria,
to be continuously reconsidered
about what we presently call 'reversibility'.

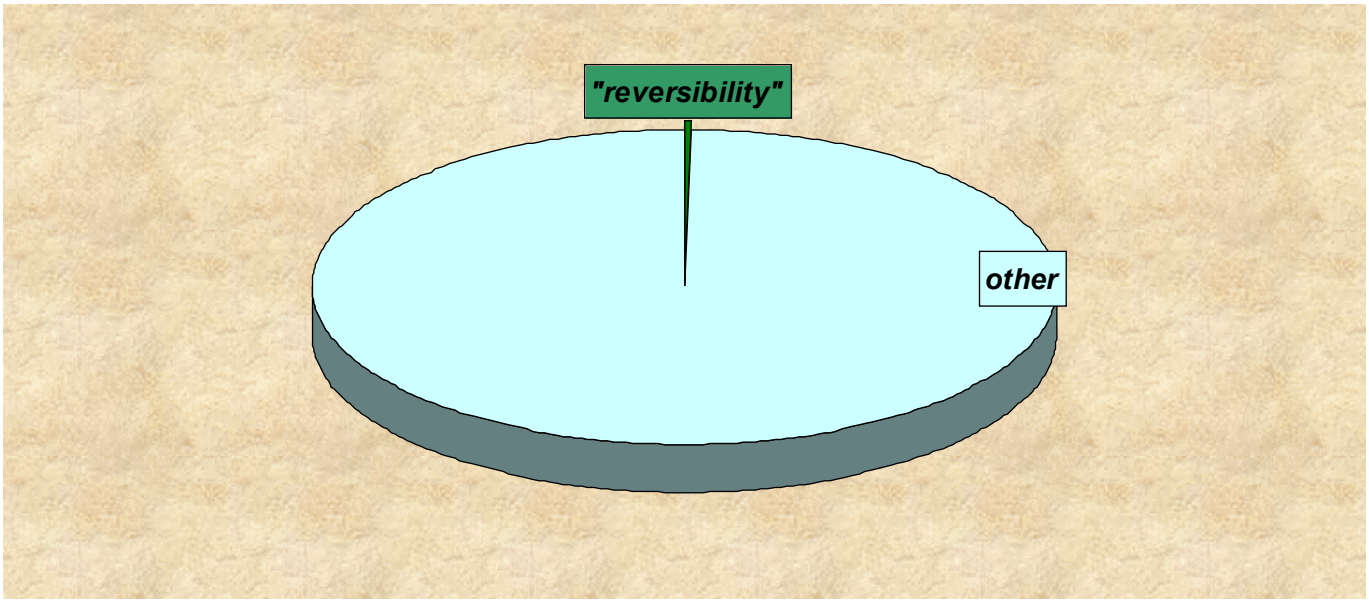
Main courses of the debate on reversibility
during the first half of our century:
Architecture
Urban environment
Anastylosis
Surface finishings and patina...

So: aesthetic and philological issues
mostly concerning what an object *means*
or how it does *appear*,
not what an object *is*.

And now?

From 1992 to 1997
only 60 of 17093 published AATA
have "reversibility" among the key words.

Theoretical debate has practically stopped during last decade.



Does it mean an achieved consciousness,
or just hiding one's head in the sand?

Reversibility: Dealing with A Ghost

Sergio Palazzi

1

Any action, *including no action*, causes an irreversible modification, to a greater or lesser extent, to the condition of any given object. Opinions which ignore this must be regarded as non-serious.

Spontaneous changes may occur because of:

- chemical degradation of intrinsically unstable materials;
- chemical, photochemical and biological aggression;
- weathering, thermal deformations, soiling;
- unbalanced mechanical tensions inside the object;
- etc.

The theory of *no intervention at all* is mystifying:
The river doesn't stop as we sit and wait on the bank.
Nature does not follow our desires.
And no man's action is reversible.

2

A large family of operations is in itself irreversible: cleaning, dirt removal, disinfecting, paper deacidification, drying of waterlogged objects, etc.

In everyday life, man-made artefacts are designed to be used as long as they are submitted to periodic maintenance and renewal.

- Should we avoid any form of cleaning or maintenance, even when this is fully justified by conservation needs and by a correct preventative design?

Or, according to a different integralism:

. Should we collect any bug along with any rug? i.e., should we preserve any alteration caused by former degradation, sooting, negligence or bad restorations?

An ancient hi-tech artefact like a Gothic building, as much as a modern engine, can only survive thanks to the endless work of technicians. They not only accept but strictly require the irreversible substitution of degraded components with new ones, which are both an original and a copy.

3

**Archaeological excavation is always irreversible,
and often crucial for future study and preservation.**

If an object has been preserved for a long time,
it must have reached an equilibrium state
with surrounding environment.

There are few things which can interfere,
In such an irreversible way,
with the story and the informations
carried by an object,
as the simple archaeological excavation
even when followed by immediate reburial.

- How many sites, discovered during XIX and XX century,
have been completely lost because of negligence,
rave tourism, war actions?

But:

- How can dogmatic supporters of *total reversibility*
allow with archaeological excavations?

4

The word reversibility concerns actions, not materials.
Materials should be referred to as, for example:
removable, long-term compatible,
not interfering with analysis or future treatments.

The lack of a clear definition of a problem
(possibly given by *figures*)

- or the simple misunderstanding
of the meaning of a word -

will surely prevent us
to find a correct solution for that problem.

Good examples proposed by German scientists dealing with architectural conservation:
Wiederreparierbarkeit, Wiederkonservierbarkeit, Wiederrestaurierbarkeit, Wiederrenovierbarkeit, Wiederergänzbarkeit...

5

**Chemical long-term compatibility between materials,
or between a substrate and a solvent used to dissolve it,
is needed but never sufficient.**

Chemical long-term compatibility is always
a *conditio sine qua non,* but only seldom is it sufficient.

Unforeseen degradation paths my arise:

... from differences in:
- water vapour permeability
- thermal expansion coefficients
- electrical conductivity;

... from phase separation after migration

... from unexpected glass transition

... etc.

And it is different to wash a resin away
from a small and polished marble test sample
or from the brittle surface of a marble relief.

Material science, the natural conjunct evolution
of engineering and physical chemistry.
can afford very useful hints.

6

No treatment should restrict an object's long-term preservation, i.e. reduce its former life expectancy.

This must be an incontrovertible position.
No one concerned with relics from the past can arbitrarily decide to subject them to treatments by which they can positively be damaged, neither through carelessness nor for commerce.

Storage, handling or exhibition are often the most dangerous 'treatments'.

Incompetence in programming these actions can negate any other conservation procedure.

Patina integralism should however be avoided.

Chemical experimentation often requires the sacrifice of non-valuable remains.
A prudential possible guideline could be: deriving testing procedures from clinical *in vivo* protocols.

7

When irreversible treatments are the sole way to save a perishing object, applied materials must have at least a longer life expectancy than the substrate.

It is always wrong to suggest
a totally 'irreversible' treatment
as the starting point of a conservation procedure.

But in many situations we have to admit
that it would be impractical or even impossible
to use so-called 'reversible' treatments.

This requires an accurate evaluation
of possible alternative materials and procedures
and of their interactions with the substrate,
always considering the foreseeable permanence
of each one as a primary issue.

Emergency rescue procedures
should be conducted by well-trained operators.

8

Potentially long-term dangerous, provisional treatments must be avoided if artefacts are not to be retreated within a fixed date.

In the case of emergency after a sudden disaster, even properly defined and executed treatments could not guarantee complete recovery.

But when there is enough time:
- to plan the activity
- to raise funds
- to know how deep and extended a conservation project can be...

... any act capable of endangering an artefact must be avoided *if there is any reasonable doubt* that the conservation work will not be completed, *and surely within the scheduled time*.

Nobody knows how many monuments, human remains, waterlogged wooden objects or flooded books have been lost because of the haste to 'recover' them, sometimes in front of a TV camera.

9

In many cases, the simple identifiability of a treatment could be enough, provided that it is not altering aesthetic and historical meanings and that faking could be excluded.

It is impossible to preserve everything
in the same optimal conditions,
not only because of limited resources,
but also on the ground of the second law.
We have to limit our pursuit of perfection.

Less significant materials do not always justify
state-of-the-art procedures
aimed to the best long term preservation
or to a complete re-treatability

The fact that a treatment is identifiable
(its *recognizability*)
should not mean a permanent disfiguration.
It is however important to define criteria
which can exclude forgery or fraud;
e.g. by the choice of undoubtedly modern materials.

10

**The widespread diffusion of technical standards,
with correctly defined, well researched
and independently verified treatment protocols,
should be a primary aim both to reasonably define
treatment potential and to avoid arbitrariness.**

Standardization is not a panacea,
but it ensures that what one is doing
in common practice
has been at least tested and verified by others,
and that a minimum agreement
on what is objectively acceptable
has been achieved,
often after keen discussions.

Standard procedures should be, as far as possible,
expressly developed for cultural heritage protection,
not merely adapted from industrial standards:
the needs are often very different
from those for which the standards were conceived.

Knowing when and how a treatment or a product
can be confidently used
will reduce the need to evoke ghosts
to guide or to freeze our actions.

11

The word ‘reversibility’ could be irreversibly banned.

We also can decide to use the name of the ghost
to designate some generic principle,
if we’re sure that it will keep aware
superstitious bleeding hearts.
But it is really necessary?
Modern thermodynamics has closed the circle,
and sciences and humanities are reaching a new common path.
Reality may be more charming than ghosts.

Now we know that we can preserve
some materials and information from the past
but at the cost of losing a greater amount
of energy and information.
We have to choose, not hide our heads in the sand.

Irreversibility is no more the companion
of the decadent hero, selfish and unpleasant,
looking at the end of its world.
It turns us into ashes, but also ashes into us.

Let’s keep our own responsibilities,
and enjoy the real world.

This paper is dedicated

to Alice Palazzi

on her first birthday

Sept. 8, 1999