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Horstmann Thermodynamics versus Mathematics_FIRST part Horstmann Errors on Thermodynamics

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Abstract
This 1st part consider what the author found in the Hortmann’s paper, translated by E. Starikov. This follows the paper “The Mathematics of Thermodynamics”, based on ideas of B. Finzi [one of the professors at Milan Politecnico] to be found in a paper published in the “Periodico di Matematiche, serie IV, vol. XIV, 1935”, related to a Caratheodory publication in “Mat. Ann., 67, 355, 1909, Berl. Ber. 39, 1935”. After an e-mail from E. Starikov about Gyula Farkas and Nikolaj Schiller the ideas of the three authors were compared in the paper “Addendum to Mathematics of Thermodynamics”, followed by “Linhart ideas on Entropy versus Classical Entropy: Proof of Linhart nonsense”.
Reading documents many errors are found…

Key words: Thermodynamic Principles, Mathematics, Entropy, SPQR

1. Introduction
In order to fully understand the argument, we ask the reader to refer to the Fausto Galetto documents “The Mathematics of Thermodynamics”, “Addendum to Mathematics of Thermodynamics”, “Linhart ideas on Entropy versus Classical Entropy: Proof of Linhart nonsense” and revise the known facts given there about the temperature, the thermal equilibrium, the transformation of energy (mechanical, kinetic, gravitational, electromagnetic, nuclear, ..., heat), the state variables and the 1st and the 2nd Principles of Thermodynamics.

We want here to show some of the fundamental ideas of E. Starikov about Thermodynamics (according to my understanding, hoping that I am right; if I am not, it depends on my poor ability to follow E. Starikov way of “teaching”)

- There are two kinds of Thermodynamics: the Conventional one and the TRUE (“Rational”) one
- There is only one Fundamental Law of Thermodynamics, NOT TWO laws
- Any physical transformation is a “continuous” battle between Energy and Obstacles/Hindrances (the war will never stop); it is related to the Newton’s Third Basic Law, according to which “For every action, there is an equal and opposite reaction.”

Using E. Starikov own words [1]… (underlining or colouring is mine…)

To sum up, we might formulate the ONLY VALID Basic Law of thermodynamics as the Law of Conservation and Transformation of Energy as follows:

To be capable of achieving any specific goal, the system ought to get the Vis Viva from the Energy Stock somehow (interactions between the system’s components), and then spend the latter to achieve the complete equilibrium with
the hindrances.

The intensity of the Obstacles/Hindrances ought to grow with the increase in the Driving Force’s intensity from its zero, whereas the latter means the zero Hindrances as well. The Hindrance should then always reach its maximum, whereas we have to properly ensure that the Driving Force is enough to equilibrate the Maximum Hindrance.

Hence, **any realistic process might run, if the corresponding system is possessed of the Energy Stock rich enough to provide the proper amounts of the Vis Viva.** In other words, the Driving Force should be capable of duly following the Hindrance till its Maximum, to finally compensate the latter. That is, the Livening Force intensity ought to be drivable to the level high enough to be capable of compensating the Hindrance at the Maximum of the latter. Thus, the permissible Maximum of the Vis Viva ought to perfectly correspond to the Maximum of the Hindrance, because the Total Energy must be constant.

The last but not the least point in the whole story is that driving the Vis Viva to its maximum would drive the Energy Stock, i.e., the potential energy, to its minimum, due to the fact that the Total Energy must be constant.

With all this in mind, we note that, on the one hand, the minimum of the potential energy corresponds to the equilibrium state of the system. On the other hand, this same state corresponds to the maximum kinetic energy and the maximum entropy. The latter both compensate each other, so that at last we arrive at the true saddle point on the Energy Hypersurface of our system.

Meanwhile, looking at the story purely mathematically, our process could bring us to the unambiguous saddle point, that is, to the minimax/maximin state of the system under study.

This is why the proper mathematics to describe the entire above story is nothing more and nothing less than just the **game theory.**

Excerpt 1. taken from a document of E. Starikov, downloaded from Research Gate

According to him there were some «True Thermodynamicists ‘widely unknown’ for their truly valuable contributions» and many false ones.

Some of the 1st set are: A. F. Horstmann, J. W. Gibbs, G. A. Linhart, …

I had the opportunity to show some nonsense of G. A. Linhart [4, 5]; E. Starikov answered that “errare humanum est”.

Now I will analyse the translation of a document of A. F. Horstmann, shown in the Appendix, and taken from [1].

Before going to A. F. Horstmann’s document let’s consider the following statements

<table>
<thead>
<tr>
<th>The last but not the least point in the whole story is that driving the Vis Viva to its maximum would drive the Energy Stock, i.e., the potential energy, to its minimum, due to the fact that the Total Energy must be constant.</th>
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</tr>
</tbody>
</table>

To analyse the statements, let’s consider a pendulum. A small ball of mass \( m \) is suspended from a string of length \( l \), fixed at point O, as in figure 0. \( \vartheta \) is the angle between the vertical line \( OH' \) and the string \( OP \), at time \( t \); \( \vartheta_t \) is the angle at time \( t=0 \); we consider, as it is usual, the whole mass concentrated in the centre of mass, and the forces applied to it; \( h \) is the height \( HH' \) of the ball (centre of mass) from the ball (centre of mass) minimum position \( H' \).
IF at time $t=0$ the angle is $\theta_0=0$, THEN the pendulum is in its equilibrium position $H'$; the force acting on the ball (centre of mass) $m \vec{g} = \vec{F}_g$ [Newton’s second law] is the gravitational force: it is counterbalanced by the stress $\vec{T}$ of the string [Newton’s third law]. The pendulum is at rest and it will not move [Newton’s first law].

If we want that the pendulum moves we must provide the ball with either an impulse or a force; let’s assume that due to that (before time $t=0$) at time $t=0$ the initial angle is $\theta_0$; on the ball acts the force $m \vec{g} = \vec{F}_g$ (the vector MP); it can be “divided” into two vectors: $\vec{F}$ tangential to the trajectory of the ball (centre of mass) and the other $\vec{F}^\perp$ orthogonal to the trajectory; it is counterbalanced by the stress $\vec{T}^\perp$ of the string [Newton’s third law]. The tangential force $\vec{F}$ causes the movement.

Figure 0. a pendulum

From Newton’s laws we can derive energetic quantities, at time $t$

- The potential energy $E_P = mgl(1-\cos \theta)$
- And the kinetic energy $E_K = mv^2/2$, which was named (in the old times) “Vis Viva”

Due to the Conservation Energy Theorem we have

$$mgl(1-\cos \theta_0) = E_P + E_K = mgl(1-\cos \theta) + mv^2/2$$

The ball speed (of the centre of mass) is

$$v = \sqrt{2gl(\cos \theta - \cos \theta_0)}$$

We notice that in the position $H'$ the energy is only kinetic (it has its maximum) while it is zero at the maximum distance with angle $\theta_0$: the energy is only potential (it has its maximum).

According to

The last but not the least point in the whole story is that driving the Vis Viva to its maximum would drive the Energy Stock, i.e., the potential energy, to its minimum, due to the fact that the Total Energy must be constant.

The Energy Stock should be at position $P$ with angles $\theta_0$ and $-\theta_0$, if we define a positive direction of the angles (from the vertical line).

In our example the Energy Supply is $mgl(1-\cos \theta_0)$ and $mgl[1-\cos(-\theta_0)]$ …

After some time, depending of various factors (the stress-strain of the string, the air around
the ball, …) the ball velocity go to 0: the pendulum rest on its equilibrium position, i.e. the ball (centre of mass) is in its minimum position \( H' \). The energy is “zero”. It a way of life!
So one has to meditate about the following:

> With all this in mind, we note that, on the one hand, the minimum of the potential energy corresponds to the equilibrium state of the system. On the other hand, this same state corresponds to the maximum kinetic energy and the maximum entropy. The latter both compensate each other, so that at last we arrive at the true saddle point on the Energy Hypersurface of our system.

We do not understand why the “equilibrium state of the system corresponds to the maximum kinetic energy”.

On the contrary, we do understand that the “equilibrium state of the system (after many oscillations) corresponds to the maximum entropy”, because the energy has been spoiled during oscillations, back-and-forth movement of a pendulum.

After this first analysis, it is important to see immediately the words of A. F. Horstmann related to his document

> … my current presentation pretends to be neither original, nor rigorous; in effect, it should boil down to nothing more than just familiarizing the interested readership with the actual meaning of the relevant equations and the proper ways of using the known hypotheses.

Excerpt 2. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

Did the reader notice that the author, A. F. Horstmann himself, shows a presentation that could be NOT “rigorous”?
I am really puzzled..

The 1st point dealt by Horstmann is

> On the one hand, heat can be transformed into work and, on the other hand, heat can be generated from motion. Hence, we conclude that heat is itself a movement, because movements themselves can be converted into work. The quantity of work, which the movement might in principle produce, is determined by the Vis Viva (Livening Force) of this movement – or, in other terms – by the kinetic energy of the movement, i.e., half the product of the squared velocity and the mass of the moving body. The same applies to the heat: A given quantity of heat corresponds to a certain amount of kinetic energy, which is, in turn, equal to the work to be produced from the mentioned quantity of heat. This is content of the first law of thermodynamics confirmed by the experience: Work and heat are equivalent.

Excerpt 3. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

Let’s analyse, step by step, some parts of Excerpt 3.

> … heat can be transformed into work and, on the other hand, heat can be generated from motion.

Surely Joule’s experiment showed that “heat can be generated from motion.”.
Surely gasoline engines show that “heat can be transformed into work”.
Surely turbojet engines show that “heat can be transformed into work (that makes an airplane to fly)”.
BUT… Horstmann’s conclusion is
Hence, we conclude that heat is itself a movement, because movements themselves can be converted into work.

Let’s rephrase the statement, in two parts:

Since (1) “movements themselves can be converted into work” then (2) “heat is itself a movement”.

There are a lot of cases showing the truth of the (1) part; on the contrary you need the kinetic theory of gases to say the (2) part.

Wind has energy (kinetic energy) when moving; its energy can be converted into work. Windmills transform the wind energy into work, to mill grain (many years ago!), to pump water, to generate electricity (in these days: “green electricity”).

Figure 1. A windmill (taken from Wikipedia)

Joule’s experiment allowed us to find that that “heat and work are equivalent transfer variables across the system’s boundary”, BUT NOT that heat can be transformed completely into work, as shown in figure 2.

Therefore the Horstmann’s statements

A given quantity of heat corresponds to a certain amount of kinetic energy, which is, in turn, equal to the work to be produced from the mentioned quantity of heat. This is content of the first law of thermodynamics confirmed by the experience: Work and heat are equivalent.

are misleading.

As a matter of fact, all the researchers (but very few) agree that the 1st Principle of Thermodynamics states the Conservation of Energy, which in Thermodynamics is written as

\[ dU = d^*W + d^*Q \]

[in differential form it is (for an infinitesimal transformation)] where

1. \( dU \) is the exact differential of the state variable \( U \) (internal energy)
2. \( d^*W \) is a differential form NOT exact of the transfer variable \( W \) (work done on the system)
3. \( d^*Q \) is a differential form NOT exact of the transfer variable \( Q \) (heat provided to the system)

For a cyclic process we have \( \int dU = 0 \).

Notice that -\( d^*W \) is the work done by the system and -\( d^*Q \) is the heat leaving the system.

This 1st principle states that a change in internal energy [a state variable] in a system can occur as a result of energy transfer by heat and by work, or by both [both are transfer variables and on the right side of the equation]; the 1st principle is essentially presented in
one form and it is very important, but it makes no distinction between processes that occur spontaneously and those that do not. The figure 2 shows what can happen in practice: *asymmetry between Work and Heat*...

Figure 2. Mechanical equivalent of heat (Joule’s experiment)

So we see that, for any system, we have two kinds of variables

- **state variables** are the variables which are able to define (describe) the *state* of a system: some are the position, the specific mass, the stress, the strain, the pressure, the temperature, the volume; there are other “variables” depending on the state variables, which are named state functions (or functions of state) as the internal energy, the enthalpy, the entropy, ... The important characteristic of all the state functions is that their differential is an “exact differential” which integrated provides the state function depending only on the state variables.

- **transfer variables** are the variables which transfer energy or material across the system’s boundary; some are heat and work, moles, ...

The 1st principle involves both kinds of variables.

Horstmann provides then the following statements

Further, *the experience teaches that not just any amount of heat can be implemented in work to the full extent, and the very fact, that in the caloric machine heat is always applied at a higher temperature, indicates that it is just the temperature that determines how much from a given amount of heat can be converted into work. We immediately rationalize the latter statement, if we take into account that while producing work out of heat the working body always expands under the influence of heat and has usually to overcome some resistant obstacles/hindrances/interferences/impediments (... etc.) during its expansion*. The extent [114] of the latter effects is clearly dependent on the actual type of the working body employed, but all of these resistant obstacles are indeed the greater the higher the applied temperature, which is in particular very clearly observable when choosing gases and vapors as the working bodies. Therefore, the work performable by the heat in such operations increases with the temperature; meanwhile, the law governing the latter increase can’t always be deduced from direct observations, because in general,
we have to work not only against the ubiquitous external resisting factors (observable obstacles/hindrances/impediments, etc.), but also against various internal resisting forces (cohesion, affinity, and/or further snags), which are in principle expected, but might in fact be inaccessible to the conventional measurements. The following considerations should first clarify the nature of the law in question; and we shall then use the same train of thoughts to draw our conclusions on the amount of work to be performed against the mentioned snags (i.e., resisting internal forces).

Excerpt 4. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

We will analyse all Excerpts, step by step, to see the important “problems”...

Let's analyse the following

... [1st part] the experience teaches that not just any amount of heat can be implemented in work to the full extent, and the very fact, [2nd part] that in the caloric machine heat is always applied at a higher temperature, indicates that it is just the temperature that determines how much from a given amount of heat can be converted into work. [3rd part] We immediately rationalize the latter statement, if we take into account that while producing work out of heat the working body always expands under the influence of heat and has usually to overcome some resistant obstacles/hindrances/interferences/impediments (... etc.) during its expansion.

The [1st part] recovers the drawback we highlighted before and the [2nd part] provides information not connected with any real system: only caloric machine is mentioned; is that a Carnot’s Engine? If it is like that, the statement is still misleading BECAUSE it is the difference of the temperatures \( T_h - T_c \) \((T_h \) (high temperature of the heat \( Q_h \) entering the system) and \( T_c \) (“cold” temperature of the heat \( Q_c \) leaving the system)) that determines the quantity of work; be careful, \( W = Q_h - Q_c \), only for a Carnot’s cycle of a Carnot’s Engine. We leave for the future the [3rd part]...........

And what about heat and temperature?
Horstmann says

Temperature of a body is the measure of the actual amount of heat present in this body, i.e., of the entire livening force/kinetic energy of the thermal motion. Importantly, at the zero points of the ordinary thermometric scales the body still ought to contain heat. Thus, in the following we shall speak only of the so-called absolute temperature, with the initial point of this scale being the one in which all the thermal motion really ceases. This zero point of the absolute temperature scale is in effect equal to -273°C, according to an assumption we shall consider in more detail later. Then, the entire livening force/kinetic energy of the thermal motion should be essentially proportional to the absolute temperature.

Excerpt 5. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

The yellow statement "Temperature of a body is the measure of the actual amount of heat present in this body" is nonsense! HEAT is measured in Joule, while TEMPERATURE is measured in Kelvin... Two different units of measurement for two different “physical entities”!!!

HEAT is a transfer variable, while TEMPERATURE is a state variable ...: they are two
types of variables.
The nonsense is recovered by the last sentence “Then, the entire livening force/kinetic energy of the thermal motion should be essentially proportional to the absolute temperature.” As a matter of fact, in Thermodynamics, $dU = mc_v dT$, at constant volume, being $c_v$ the specific heat at constant volume and $m$ the mass of the body.
By the way, the name specific heat is an unfortunate holdover from the days when thermodynamics and mechanics developed separately. A better name would be specific energy transfer, but the existing term is too entrenched to be replaced.
Moreover the statement “amount of heat present in this body” is a physical nonsense! As a matter of fact consider the following:

When you heat a substance, you are transferring energy into it by placing it in contact with surroundings that have a higher temperature (when you place a pan of cold water on a stove burner. The burner is at a higher temperature than the water, and so the water gains energy by heat).

Notice what heat is not in the following common quotes.
(1) Heat is not energy in a hot substance. For example, “The boiling water has a lot of heat” is incorrect; the boiling water has internal energy $U$.
(2) Heat is not radiation. For example, “It was so hot because the sidewalk was radiating heat” is incorrect; energy is leaving the sidewalk by electromagnetic radiation.
(3) Heat is not warmth of an environment. For example, “The heat in the air was so oppressive” is incorrect; on a hot day, the air has a high temperature $T$.

As an analogy to the distinction between heat and internal energy, consider the distinction between work and mechanical energy. The work done on a system is a measure of the amount of energy transferred to the system from its surroundings, whereas the mechanical energy (kinetic energy plus potential energy) of a system is a consequence of the motion and configuration of the system. Therefore, when a person does work on a system, energy is transferred from the person to the system. It makes no sense to talk about the work of a system; one can refer only to the work done on or by a system when some process has occurred in which energy has been transferred to or from the system. Likewise, it makes no sense to talk about the heat of a system; one can refer to heat only when energy has been transferred as a result of a temperature difference. Both heat and work are ways of transferring energy between a system and its surroundings.

Let’s go on. Later we find

\[
\text{If we imagine that the thermal motion is in effect carried out by the smallest particles of the body under study, the livening force/mean kinetic energy of such particle motions should then also be proportional to the temperature; Thus, the particles move with certain speeds determined by the temperature, in following certain [115] trajectories dependent on the actual physical state of the other body. For example, the trajectories of the oxygen and hydrogen atoms will be exhibiting different designs, if they are pertinent to solid, liquid or gaseous water or just to a gas mixture of chemically unbound oxygen and hydrogen. As a consequence, the different physical-chemical properties exhibited by the same chemical substance in these various physical-chemical/aggregate states are due to the different shapes of the trajectories in question; conversely, the shape of the atomic trajectories ought to fully reflect the manner in which the atoms are chemically bonded, and thus determine what is the actual physical state of the body to which they belong, but not the speed of these atoms.}
\]

Excerpt 6. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)
Does the reader find the errors in the following statements?

… livening force/mean kinetic energy of such particle motions should then also be proportional to the temperature; Thus, the particles move with certain speeds determined by the temperature,…

To understand we need to speak about the “kinetic theory of gases.”

Let’s consider N molecules of an ideal gas contained in a tank of volume V with boundary ω [the gas consists of a number of identical molecules (which we imagine to be point-like); the number of molecules in the gas is large, and the average separation between them is large compared with their dimensions. Therefore, the molecules occupy a negligible volume in the tank container]. We assume that

A. The molecules obey Newton’s laws of motion, but as a whole their motion is isotropic: any molecule can move in any direction with any speed.

B. The molecules interact only by short-range forces during elastic collisions. The molecules exert no long-range forces on one another.

C. The molecules make elastic collisions with the boundary ω.

Every molecule (of mass $m_0$) has speed (vector) $\vec{v}$; then its linear momentum is $m_0 \vec{v}$; as the molecule collides elastically with the boundary ω [property C above], its velocity component perpendicular $v_n$ to the boundary [\text{\mathbf{n}} is the normal vector to the boundary \text{ω}] is reversed because the mass of the boundary is far greater than the mass of the molecule: the impulse from the boundary ω causes a change in the molecule’s momentum. Using Newton’s second law of motion, we can relate the linear momentum of a particle to the resultant force acting on the particle (the mass $m_0$ is assumed to be constant): the time rate of change of the linear momentum of a particle is equal to the net force acting on the particle. Because the momentum component of the molecule is $m_0 v_n$ before the collision and $-m_0 v_n$ after the collision, the change in the normal component of the momentum of the molecule is $-2m_0 v_n$ and then the “mean” force exerted on the boundary is $F_{\text{molecule}} = -2m_0 v_n/\Delta t$ where $\Delta t$ is the time between collisions of the molecule with the boundary (\Delta t varies between the molecules): the boundary reacts with an opposite force (Newton’s Third Law of Mechanics). For a very large number of molecules such as Avogadro’s number, however, these variations in force are smoothed out so that the average force given above is the same over any time interval. Therefore, the constant force $F$ on the wall due to the molecular collisions is hence the total “mean” force exerted on the boundary $F = -2m_0 v_n/\Delta t$; there is then a force on the boundary ω due to the N molecules hitting the boundary: the ratio of the “total” force to the area of the surface of the boundary is the pressure of the gas.

We provide here only the result (not the complete theory); the pressure of the gas is

$$p = \frac{2}{3} \left( \frac{N}{V} \right) \left( \frac{1}{2} m_0 \overline{v^2} \right)$$

where $m_0 \overline{v^2}/2$ is the translational kinetic energy per molecule; usually, molecular rotations or vibrations have no effect on the motions considered here. When the molecule hits the boundary of the tank it transfers energy to the boundary. Then the pressure $p$ depends on the mean value of the kinetic energy...

Since for ideal gases we have the state equation

$$f(p, V, T) = 0$$

from the two equations we derive

$$\frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} kT \quad (*)$$

where $k$ is the Boltzmann’s constant.
What does the formula (*) mean?
That kinetic energy depends on the temperature?
**OR** that temperature depends on the kinetic energy?
The SECOND one!
**Temperature depends on** the kinetic energy!!!
When we provide heat to a system, we provide energy which is transferred to the molecules of the gas!!!
We do not provide “temperature” ………….
Heating a cube of ice we melt the ice, we DO NOT provide “temperature” to the ice [which remains fixed until the whole ice is melted] !!!
Then

\[ \text{... the particles move with certain speeds determined by the temperature,....} \]

is wrong!
It is instead **true** that

\[ \text{... the temperature is determined by the speeds of the particles...} \]

Obviously it is wrong also the following statement

\[ \text{Therefore, we might safely assume, that the average livening force/kinetic energy of the atoms and, consequently, their average speed [116] is dependent on the temperature only and never on the shape of the trajectories followed by the atoms follow during their movements.} \]

Excerpt 7. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

The paper of Bruno Finzi “Cosa è la temperatura (what is the temperature)” *Periodico di Matematiche, serie IV, vol. XIV* and *Academia.edu* is very clear on this point: difference between temperature and kinetic energy.
From formula (*) we know that the mean kinetic energy (livening force, Vis Viva) and the temperature are correlated. **BUT** correlation does not mean causation.

*All that is clear using properly Mathematics.*

Again on kinetic energy and temperature (Horstmann’s ideas)

\[ \text{... The actual nature of these forces, as well as the shape of the resulting trajectories, are practically unknown to us, but, as to the amount of the forces involved, we might nonetheless plausibly assume that at any given moment of the time and at any point of a particular atomic trajectory they ought to boil down to the centrifugal force generated by the movement, for otherwise the atom would just have to leave its actual trajectory. Then, for a circular movement the centrifugal force is } \frac{mv^2}{R} \text{, where } m \text{ stands for the mass, } v \text{ – for the velocity of the atom and } R \text{ – for the radius of our imaginary circle. The atomic trajectories are in reality not necessarily circular; but whatever the actual shape they could acquire, we might always take the actual atomic orbit into such small sections that each of the latter in its entire length might be coincident with a circle (called the curvature circle), whose radius is equal to } r \text{. Then, at this particular point of the trajectory, the centrifugal force is } \frac{mv^2}{r} \text{. If the velocity of the atom gets greater due to the increase in temperature, e.g., it’s now about } v_1 > v \text{, then so does the centrifugal force, and – therefore – all the other forces ought to grow as well, if they still have to hold the atom within its actual orbit. If we denote such forces by } k \text{ and } k_1 \text{, we arrive at the following expressions:} \]
\[ k = \frac{mv^2}{r}; \quad \text{and} \quad k_i = \frac{mv_i^2}{r}; \quad \text{(1)} \]

And finally we get:
\[ \frac{k}{k_i} = \frac{mv^2}{mv_i^2}; \quad \text{(2)} \]

[117] that is, the interrelationship among such forces ought to safely mimic the one among the actual livening forces/kinetic energies of the atoms. This applies to each atom at each point of its trajectory. Since only the average livening force/kinetic energy of the atoms should be proportional to the temperature, we should also conclude that the actual inter-atomic forces must increase in proportion to the temperature as well.

Excerpt 8. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

If the velocity of the atom gets greater due to the increase in temperature, is wrong, as it was (before) the sentence

… the particles move with certain speeds determined by the temperature,…

NOTICE the difference between Excerpt 8 and what we said about kinetic energy before: there the kinetic energy was translational with hits against the boundary of the tank, while here (in the Excerpt 8) the energy is rotational!!! This has nothing to do with pressure on the boundary and then with… The speed \( v \) (in the Excerpt 8) has nothing to do with the velocity \( v \) in our previous comments!

According to the Quantum Mechanics, providing heat (and consequently increasing the temperature) the atoms can increase their rotations and vibrations. As more heat is transferred (and then temperature is raised) rotations and vibrations contribute more to the internal energy \( U \) (made of translational, rotational and vibrational energies). …

Since only the average livening force/kinetic energy of the atoms should be proportional to the temperature, we should also conclude that the actual inter-atomic forces must increase in proportion to the temperature as well.

is wrong as were wrong the previous considered statements; see formula (\(^*\)).

Heating, the process of transferring energy across the boundary of a system, modifies the internal energy which includes both the kinetic energy (of random translation, rotation and vibration of molecules) and vibrational potential energy (within the molecules) with vibrational potential energy (between the molecules).

Internal energy is associated (= correlated) with the temperature and the physical state (solid, liquid, gas) of the system.

The internal energy increase, of any sample of a substance, is related to the specific heat \( c = Q/(m\Delta T) \) of the substance, per unit mass. \([Q=\text{heat}, m=\text{mass}, T=\text{temperature}]\).

Temperature DOES NOT cause Heat…. Temperature difference \( \Delta T \) causes flow of the energy (that we name heat), but DOES NOT cause Heat….

Finally we arrive to the end of this “very long” introduction… [Horstmann’s ideas]

Summing up all the above, we stress that the temperature increase ought to trigger the change of physical state, whereas the atoms ought to leave their previous orbits, if there would be no simultaneous increase in the resistant factors/forces tending to preserve the atoms in their current trajectories. And, as soon as the resistance in question stems from the inter-atomic forces only, there is no way to change anything. Still, according to the experience in many
cases, the external pressure supports the internal forces holding together the atoms in the system in their resistance against the heat-induced forces driving the atoms apart from each other, and the magnitude of the external pressure might be arbitrarily variable. The latter fact, e.g., allows preventing the evaporation of liquids by increasing the external pressure despite an elevated temperature. And, as the experiments triggered the present communication clearly show, the same holds for heat-induced desorption of absorbed gases, escape of the crystalline water, decomposition of chalk and of the ammonium-chloride compounds, etc. It is for the present all the same, how exactly the external pressure acts on the orbits of individual atoms; but, if the latter effect takes place and if it is possible to prevent a change of physical state by increasing the external pressure along the temperature growth, then we know from the foregoing that the pressure-induced resistance to this particular change of physical state must anyway grow in the same proportion as the temperature.

Let's see the statements

Summing up all the above ...

... temperature increase ought to trigger the change of physical state ...

... according to the experience in many cases, the external pressure supports the internal forces holding together the atoms in the system in their resistance against the heat-induced forces driving the atoms apart from each other, ...

... how exactly the external pressure acts on the orbits of individual atoms; but, if the latter effect takes place and if it is possible to prevent a change of physical state by increasing the external pressure along the temperature growth, then we know from the foregoing that the pressure-induced resistance to this particular change of physical state must anyway grow in the same proportion as the temperature.

If energy is transferred by heat to a system at constant volume, no work is done on the system. Hence for the 1st Principle of Thermodynamics (for n moles) dU = d*Q = nCv dT where Cv is the specific heat, at constant volume, per mole.

If the pressure is kept constant, at a high value p, and energy is transferred by heat to a system at constant pressure, we have d*Q = nCp dT = dU – d*W, where Cp is the specific heat, at constant pressure, per mole.

For elastic bodies the internal energy (per unit of volume), at a stated temperature [see the document “The Mathematics of Thermodynamics”, based on ideas of B. Finzi], is the elastic energy whose differential is [6] (using the tensorial notation)

\[ dU = -p_{ik} d\xi_{ik} = -c_{ikrs} \xi_{rs} \xi_{ik} \]

whose integral is

\[ U = -c_{ikrs} \xi_{rs} \xi_{ik} / 2 + \text{const} \]

For isotropic bodies the 4-tensor c_{ikrs} is very simple and so is the internal energy.

For a fluid, the stress tensor is given by a simple function, the pressure \( p=p(P), \ p(n)=pn \), whichever is the normal vector \( n \), which means \( p_{ik} = p \delta_{ik} \) [\( \delta_{ik} \) is the Kronecker symbol, \( \delta_{ik}=0 \) for \( i\neq k \) and \( \delta_{ik}=1 \) for \( i=k \)].

If we provide the quantity of heat \( d^*Q \), to the body, we modify (increase) the \( \xi_{ik} \) strain (deformation) tensor field and then we increase the internal energy \( U \) [mean kinetic energy]; however, if we increase the external pressure on the body we increase the tensor...
\( p(n) = p \) and modify (reduce) the \( \xi^{ik} \) strain (deformation) tensor field, in the opposite way…

Therefore, by increasing the external pressure on the body we need more quantity of heat \( d^*Q \) to be added, to the body, in order to keep the \( \xi^{ik} \) strain (deformation) tensor field constant. Hence, if we keep at high levels the external pressure we must provide more and more quantity of heat to the body, **NOT more and more temperature**!!

The statement

\[ \text{... temperature increase ought to trigger the change of physical state ...} \]

Is misleading, **BECAUSE** the quantity of heat \( Q \), provided to the body, increases the \( \xi^{ik} \) strain (deformation) tensor field and the internal energy \( U \) [mean kinetic energy] up to the change of physical state, where the temperature remains constant till the change of physical state is completed: during the whole change of physical state the internal energy \( U \) is continuously increasing. When the change of physical state is completed, the internal energy \( U \) increases again **and** the temperature increases again, by adding new (other) quantity of heat \( Q \).

From formula (\*) we know that the mean kinetic energy (livening force, Vis Viva) and the temperature are correlated. **BUT** correlation does not mean causation.

*All that is clear using properly Mathematics.*

### 2. ENTROPY by Horstmann

Now we come where Horstmann goes to the 2\textsuperscript{nd} Principle of Thermodynamics.

Here we have some formulae to consider, not only statements as before!!!

Any change of state \([118]\) preventable by external pressure might be arbitrarily observable at various temperatures, but one solely has to let the pressure be so high that the resistance to the heat-induced change of the physical state might still be overcome at this particular temperature.

With all this in mind, the work to be performed in the latter case is definitely growing along with the resistance; because the other factor, namely the way, which the atoms have to lay back, remains just the same.

Then, it follows from what we know about the resistance that the **whole amount of work done by the heat at any change of the body’s physical state ought to be proportional to absolute temperature at which this particular change occurs.**

And this is just the law we are seeking for, which must anyway be carrying the name of Clausius\(^4\), who was undoubtedly pioneering its actual formulation.

\(^4\) It should be mentioned here, how to formally get to the law by Rudolf Clausius starting from the ordinary form of the Second Basic Law of thermodynamics. The analytical expression of the latter conveys that for a reversible cyclical process the following is true \( \frac{dQ}{dT} = 0 \); Then, the quantity of heat supplied to the body ought to be a function of two variables, one of which is the absolute temperature \((T)\) itself, and the other \((x)\), which should determine the form of the atomic paths. It is then possible to write \( dQ = Xdx + CdT \) and to satisfy the latter equation according to the rules of differential calculus. We get the following expression as a result:
\[
\frac{d}{dT} \left( \frac{X}{T} \right) = \frac{d}{dx} \left( \frac{C}{T} \right) ; \tag{3}
\]

or after consequently performing the operation of differentiation:

\[
T \frac{dX}{dT} - X = T \frac{dC}{dx} ; \tag{4}
\]

The above equation should, among other things, take into account that the following statements are simultaneously true:

\[
T \frac{dX}{dT} - X = 0 \text{; and } T \frac{dC}{dx} = 0 . \tag{5}
\]

The second of the expressions (5) corresponds to the condition given by us – namely that the amount of heat actually existing in the body \cite{119} is not dependent on the atomic/molecular arrangement, while the first of the expressions (5) gives by integration \( X = T \text{ Const} \), which is nothing more and nothing less than just the Clausius' law, because \( X \) is the amount of heat transformed into the work during the change of \( x \) to \( dx \). (See e.g. Clausius, Abhandlungen I, 264). This is exactly the context I have pointed out on another occasion (Berichte der Deutschen chemischen Gesellschaft, II, 726).

Excerpt 10. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

As done before, we analyse Excerpt 10, step by step...

Then, it follows from what we know about the resistance that the whole amount of work done by the heat at any change of the body's physical state ought to be proportional to absolute temperature at which this particular change occurs.

Horstmann and Starikov connect entropy to """"resistance""""...

I must admit that I DO NOT understand the statement that the whole amount of work done by the heat at any change of the body's physical state ought to be proportional to absolute temperature at which this particular change occurs.

Let's consider a system made of a cube of ice [of mass \( m \)] and water [of mass \( m_i \)] at 0 °C (two phases in equilibrium); now imagine that an amount of energy \( Q \) [heat] enters the system and after a certain time the water mass is \( m_i \), due to melting. If the ice cube is completely melted, after a time, we see only one phase (water) the mass of water is \( m_f = m_i + m \) and the quantity \( Q \) is given by the product \( L_f m \), where \( L_f \) is the latent heat (of fusion).

\( Q \) is proportional to 273.14 °C. \( Q = m \times 333 \) J.

BUT there was any work during fusion?

Reader, please, answer....

There was only increment of Internal Energy \( U \)...

Let's consider a system made of water [of mass \( m_f = m_i + m \)] at 0 °C (one phase); now imagine that energy \( Q \) enters the system and after a certain time the water mass \( m_i \) goes to 100 °C; at this point the water evaporates by adding new quantity of heat (we start to have two phases in equilibrium; water and steam); we added a quantity of heat \( Q = m_i \times 419 \) J.

Adding heat the water evaporates and the system is at 100 °C. The water–steam mixture remains at 100.0°C --even though energy is being added-- until all the liquid has been
converted to steam: we see only one phase (steam at 100 °C), whose mass is still \( m = m_i + m \). The energy required to convert \( m = m_i + m \) of water to steam at 100.0°C is the quantity \( Q \) given by the product \( L \cdot m \), where \( L \) is the latent heat (of vaporisation).

\[ Q \text{ is proportional to } 373.15 \text{ °C}. \quad Q = m_i \cdot 2260 \text{ J}. \]

BUT there was any work during vaporisation? Reader, please, answer….

Since Helium melts at a pressure of 2.5 MPa, \( Q \) depends on the pressure and on the temperature…

During fusion and vaporization there was no work. During fusion and vaporization the internal energy increased.

PERHAPS the **whole amount of work done by the heat at any change of the body’s physical state...** has to be considered as equivalent to **all internal energy increase**…

SURELY, the ratio of the energy \( Q \) and the absolute temperature \( T \), (constant) during the phase change is important: actually, \( Q/T \) is a fundamental **state function**.

And now Clausius enters the stage…

... And this is just the law we are seeking for, which must anyway be carrying the name of Clausius\(^1\), who was undoubtedly pioneering its actual formulation.

\(^1\) It should be mentioned here, how to formally get to the law by Rudolf Clausius starting from the ordinary form of the Second Basic Law of thermodynamics. The analytical expression of the latter conveys that for a reversible cyclical process the following is true \( \frac{dQ}{dT} = 0 \); ….

Perhaps there were at least **two typing errors** (??); "analytical expression of the Second Basic Law of thermodynamics for a reversible cyclical process

\[ \int \frac{dQ}{T} = 0, \quad \text{NOT} \quad \frac{dQ}{dT} = 0 \ldots!!\]"

and one Mathematical/Physical Nonsense:

\[ \frac{dQ}{dT} = 0 \quad \text{entails that } Q \text{ is constant, versus temperature}!!! \]

and one Physical Nonsense:

\[ \frac{dQ}{dT} = C = 0 \quad \text{heat capacity equal to ZERO} ??? \]

All that is clear using properly Mathematics.

What about the following?

Then, the quantity of heat supplied to the body ought to be a function of two variables, one of which is the absolute temperature \( (T) \) itself, and the other \( (x) \), which should determine the form of the atomic paths.

It is then possible to write \( dQ = Xdx + CdT \) and to satisfy the latter equation according to the rules of differential calculus.

We get the following expression as a result:
\[ \frac{d}{dT} \left( \frac{X}{T} \right) = \frac{d}{dx} \left( \frac{C}{T} \right) ; \quad (3) \]

or after consequently performing the operation of differentiation:

\[ T \frac{dX}{dT} - X = T \frac{dC}{dx} ; \quad (4) \]

**Horstmann does not tell us what C is...!!!** Perhaps it is the heat capacity ... He only talks about ""... (x), which should determine the form of the atomic paths."", a statement that is a complete NONSENSE!

From \( dQ = Xdx + CdT \) anybody DOES NOT get the ""result"" (3), UNLESS he says that the ratio \( \frac{d^*Q}{T} \) MUST be an exact differential

\[ \frac{dQ}{T} = \frac{X}{T} dx + \frac{C}{T} dT = M(X,T)dx + N(X,T)dT \]

which, **mathematically, entails** that

\[ \frac{\partial M(X,T)}{\partial T} = \frac{\partial N(X,T)}{\partial x} \]

**Horstmann does not tell us... because he does not write** \( \Phi \frac{dQ}{T} = 0 ...!!! \)

HE writes \( \frac{dQ}{dT} = 0 ; ...!!! \)

Let the unit vectors \( i \) and \( j \) in the plane \( X, T \) and \( \Phi(X, T) \) the integral of \( d^*Q/T \), then the gradient is

\[ \text{grad}(\Phi) = \frac{\partial \Phi}{\partial X} i + \frac{\partial \Phi}{\partial T} j = M(X,T)i + N(X,T)j \]

If \( k \) is the unit vector orthogonal to the plane \( X, T \) [and to the unit vectors \( i \) and \( j \)] there exists another vector, named rotation (or curl), and written \( \text{rot}\Phi(X, T) \), defined by

\[ \text{rot}[M(X,T)i + N(X,T)j] = \left( \frac{\partial \Phi}{\partial X} - \frac{\partial \Phi}{\partial T} \right) k = \left( \frac{\partial N(X,T)}{\partial x} - \frac{\partial M(X,T)}{\partial T} \right) k \]

When two independent thermodynamic variables are considered, there is ALWAYS a vector such that \( \text{rot}[M(X,T)i + N(X,T)j] = 0 \) which entails the existence of the **integrating factor** \( 1/\tau(X,T) \).

In the case considered the **integrating factor** is \( 1/T \), where \( T \) is the absolute temperature [2, 3]

**This result is very important because it holds for any number n of Independent thermodynamic variables, n>2, defining an equilibrium thermodynamic state of any system.**

AGAIN, all that is clear using properly Mathematics.

The following development is again a **nonsense**..

The above equation should, among other things, take into account that the following statements are **simultaneously true**:

\[ T \frac{dX}{dT} - X = 0 ; \quad \text{and} \quad T \frac{dC}{dx} = 0 . \quad (5) \]

The second of the expressions (5) corresponds to the condition given by us – namely that **the amount of heat actually existing in the body** [119] is not dependent on the atomic/molecular arrangement, while the first of the
expressions (5) gives by integration $X = T \text{ Const}$, which is nothing more and nothing less than just the Clausius’ law, because $X$ is the amount of heat transformed into the work during the change of $x$ to $dx$. (See e.g. Clausius, Abhandlungen I, 264). This is exactly the context I have pointed out on another occasion (Berichte der Deutschen chemischen Gesellschaft, II, 726).

The two formulae (5) are nonsense………………

For, if they are both 0, then
$$\frac{\partial M(X,T)}{\partial T} = \frac{\partial N(X,T)}{\partial x} = 0,$$
and therefore $d^*Q/T=0$, there is a constant transfer of heat!!!

**IS THAT true for all thermodynamic transformations???

I do not think so!!!

IF $T \frac{dx}{dT} - X = 0$ THEN $X=T$*constant; hence $X/T=constant$ and since “$X$ is the amount of heat transformed into the work during the change of $x$ to $dx$” we have that the ratio of HEAT/TEMPERATURE is constant!!!

**IS THAT true for all thermodynamic transformations???

I do not think so!!!

Only isothermal transformations show the ratio of HEAT/TEMPERATURE constant!!!

Moreover, mathematically, the “…change of $x$ to $dx$” makes no mathematical sense; it MUST BE “…change of $x$ from $x$ to $x + dx$”

All that is clear using properly Mathematics.

Moreover the statement

| the amount of heat actually existing in the body [119] |

is a physical nonsense…

Heat is a transfer variable!!! There is no heat in a body!!!

As said before (repeated here!!!), infact consider the following:

When you *heat* a substance, you are transferring energy into it by placing it in contact with surroundings that have a higher temperature (when you place a pan of cold water on a stove burner. The burner is at a higher temperature than the water, and so the water gains energy by heat).

Notice what heat is *not* in the following common quotes.

(1) Heat is *not* energy in a hot substance. For example, “The boiling water has a lot of heat” is incorrect; the boiling water has *internal energy* $U$.

(2) Heat is *not* radiation. For example, “It was so hot because the sidewalk was radiating heat” is incorrect; energy is leaving the sidewalk by *electromagnetic radiation*.

(3) Heat is *not* warmth of an environment. For example, “The heat in the air was so oppressive” is incorrect; on a hot day, the air has a high *temperature* $T$.

As an analogy to the distinction between heat and internal energy, consider the distinction between work and mechanical energy. The work done on a system is a measure of the amount of energy transferred to the system from its surroundings, whereas the mechanical energy (kinetic energy plus potential energy) of a system is a consequence of the motion and configuration of the system. Therefore, when a person does work on a system, energy is transferred from the person to the system. It makes no sense to talk about the work *of* a system; one can refer only to the work done *on* or *by* a system when some process has occurred in which energy has been transferred to or from the system. Likewise, *it makes no sense to talk about the heat of a system*; one can refer to heat only when energy has been transferred as a result of a temperature difference. Both heat and work are ways of transferring energy between a system and its surroundings.
And IF the word work should be actually the internal energy U...?

Let’s go on trying to fill with the symbol ““”“holes ““”“ in the Horstmann’s text.

To express [119] the law in an equation, let us assume that the total work to ensure a particular change of the physical-chemical state (e.g., the evaporation of a quantity of water) at the temperature $T$ is equal to $W$, so that $\delta W$ would be the increase in this work when the temperature increases up to $T + \delta T$. Then, according to the law under study, we get:

$$\frac{W}{W + \delta W} = \frac{T}{T + \delta T} \quad \text{oder:} \quad (1) \quad W = T \frac{\delta W}{\delta T}.$$  

(6)

Meanwhile, the total work $W$ ought to consist of two parts, which might be viewed separately. The amount of work against internal forces is, say, $J$, and its amount isn’t known to us for the present, but it is plausible to assume that such a work amount should be conserved for one and the same change of the physical state at different temperatures; indeed, the way/trajectories the atoms have to cover/follow remain the same, and the internal forces are not temperature-dependent, if the spacing between the atoms remains the same. Strictly speaking, the forces under study might surely change in effect, because it’s not possible to completely prevent any inter-atomic arrangement alteration by applying the external pressure, but it is nonetheless possible to arrange for the temperature change $\delta T$ to be always so small that the inner work remains noticeably the same. The increase in the total work might then arise solely out of the increase in the external work. Bearing this in mind, we denote here $E$ to be the work against the external pressure, so that $\delta E$ would then be its increase resulting from the temperature increase $\delta T$ – and finally we get:

$$W = E + J \quad \text{and:} \quad \delta W = \delta E.$$  

As a result, the equation (2) in (6) [120] turns into:

$$W = E + J = T \frac{\delta E}{\delta T}.$$  

(7)

(8)

Excerpt 11. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

Let’s analyse, as usually, the Excerpt 11, step by step...

To express [119] the law in an equation, let us assume that the total work to ensure a particular change of the physical-chemical state (e.g., the evaporation of a quantity of water) at the temperature $T$ is equal to $W$, so that $\delta W$ would be the increase in this work when the temperature increases up to $T + \delta T$. Then, according to the law under study, we get:

$$\frac{W}{W + \delta W} = \frac{T}{T + \delta T} \quad \text{oder:} \quad (1) \quad W = T \frac{\delta W}{\delta T}.$$  

(6)

Let’s consider a mass=1 kg of water, initially at 25 °C, in a cylinder, fitted with a movable piston; firstly we maintain the piston in a fix position and we heat the water until it boils and evaporates at 373.15 °C (at this time the temperature stays constant, until all the water evaporated); since the volume remains constant there is no work done. IF we heat again, until all the water evaporated, the temperature increases and no work is done in spite of pressure increase, during the physical change from liquid water to vapor. Then there is no ““”“total work to ensure a particular change of the physical-chemical state
Perhaps, as said above, the "total work $W$ ... at the temperature $T$..." has to be considered as the internal energy $U...$, because during the "particular change of the physical-chemical state (e.g., the evaporation of a quantity of water) at the temperature $T$" the kinetic energy of molecules (internal energy) increases in order to have the evaporation.

Let's go on in our analysis...

Meanwhile, the total work $W$ ought to consist of two parts, which might be viewed separately. The amount of work against internal forces is, say, $J$, and its amount isn't known to us for the present, but it is plausible to assume that such a work amount should be conserved for one and the same change of the physical state at different temperatures; Indeed, the way/trajectories the atoms have to cover/follow remain the same, and the internal forces are not temperature-dependent, if the spacing between the atoms remains the same. Strictly speaking, the forces under study might surely change in effect, because it's not possible to completely prevent any inter-atomic arrangement alteration by applying the external pressure, but it is nonetheless possible to arrange for the temperature change $\Delta T$ to be always so small that the inner work remains noticeably the same.

Does the reader see that Horstmann is self-contradicting with the statement...

that the whole amount of work done by the heat at any change of the body's physical state ought to be proportional to absolute temperature at which this particular change occurs.

which I had to admit that I DID NOT understand ????????

In F. Galetto’s opinion, the whole amount of work and the total work $W$ should be the same concept.
We saw that for ice melting and later for water evaporation only internal energy was changing due to heat.

According to the 1st Principle of Thermodynamics (Conservation of Energy) which in Thermodynamics (that we find in these days) is written as
\[ \Delta U = W + Q \]

for a finite transformation, where

- \( \Delta U \) is the variation of the state variable \( U \) (internal energy)
- \( W \) is the transfer variable \( W \) (work done on the system)
- \( Q \) is the transfer variable \( Q \) (heat provided to the system)

In F. Galetto’s opinion (hoping he is right)
- referring to figure 4, where the system (cylinder and piston) is initially full of water and, by heating, later the two phases water-steam do the work \( E \) through the piston movement against the external pressure
- using the Horstmann’s notations, we have to write the 1\textsuperscript{st} Principle of Thermodynamics as

\[ W = E + J \]

for a finite transformation, where

- \( J \) is the variation of the state variable internal energy \([\Delta U \text{ above}]\)
- \( E \) is the transfer variable work done by the system \([- W \text{ above}]\)
- \( W \) is the transfer variable heat provided to the system \([Q \text{ above}]\)

Figure 4. a cylinder, fitted with a movable piston, at boiling temperature of water…

The following is NONSENSE

... but it is nonetheless possible to arrange for the temperature change \( \Delta T \) to be always so small that the inner work remains noticeably the same.

It is known that the internal energy (inner work for Horstmann) is related to the kinetic energy of the molecules and this is related to the temperature \( T \); so heating, with \( d^\ast Q \) amount of heat, causes a temperature change \( dT \) and an increment of internal energy (inner work for Horstmann) so that it is false to say that

... the inner work remains noticeably the same.

And …. What about the following???

The increase in the total work might then arise solely out of the increase in the external work. Bearing this in mind, we denote here \( E \) to be the work against the external pressure, so that \( \Delta E \) would then be its increase resulting from the temperature increase \( \Delta T \) – and finally we get:
As a result, the equation (2) in (6) \[120\] turns into:

\[ W = E + J = T \frac{\delta E}{\delta T}. \] (8)

The formula (7) above is wrong BECAUSE it does not satisfy the 1st Principle of Thermodynamics:

\[ \delta W = \delta E + \delta J \]

Reader, is the formula (8) sound?

3. **STOP of the analysis of Horstmann’s paper**

I can stand it any longer to find errors in the Horstmann’s paper…

I leave the pursue for future…

In any case I provide the parts to be analyzed: 3 more parts.

After this NOT analyzed section, I will consider in the 4th section the ideas of E. Starikov.

The new part filled with the symbol "" holes "" in the text.

**From now on we shall deal with such changes of physical state that are accompanied by some gas formation.** Let us then imagine some body enclosed in a cylinder with a movable punch, so that the external pressure should be brought about by some weights placed on the upper surface of this punch. In generating the external pressure to be just overcome at the temperature \( T \), we have to charge the punch with \( p \) units of weight; hence, if the upper surface of the punch is equal to \( f \), then an increase of the gas volume inside the cylinder would lift the weight \( pf \) to a certain height \( h \). Therefore, the external work to perform the latter movement could be cast as follows:

\[ E = pfh = p \delta v, \] (9)

where \( \delta v \) stands for the increase in volume during the change of the physical state. If we denote \( p + \delta p \) the external pressure corresponding to the temperature \( T + \delta T \), then we arrive at the following statement:

\[ E + \delta E = (p + \delta p) \delta v, \] (10)

And consequently:

\[ \delta E = \delta p \cdot \delta v. \] (11)

Excerpt 12. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

The new part filled with the symbol "" holes "" in the text.

**Using the above results for \( E \) and \( \delta E \) the equation (8) might be recast as follows:**

\[ W = p \delta v + J = T \frac{\delta p}{\delta T} \delta v. \] (12)

And for the inner work we therefore get:

\[ J = \left( T \frac{\delta p}{\delta T} - T \right) \delta v. \] (13)

Finally, to mathematically formulate the equation under study in entirely strict
manner we have to replace the expression \( \frac{\delta p}{\delta T} \) by the true derivative of the pressure \( p \) at the temperature \( T \), that is, by \( \frac{dp}{dT} \) – because, as already noted, the smaller \( \delta T \), the exacter would be the equation for the infinitely small temperature changes.

Remarkably, any measurement of the inner work could be possible solely via determining the amount of heat spent for carrying out the work of interest, and \[121\] therefore we have to bring the equations just derived into a usable form by multiplying them with the caloric equivalent of work = \( A \). Thus, we obtain as a result:

\[
Q = AT \frac{\delta p}{\delta T} \delta v . \tag{14}
\]

\[
Q_1 = A \left( T \frac{\delta p}{\delta T} - p \right) \delta v . \tag{15}
\]

\( Q \) stands here for the amount of heat to be transformed into work during the physical state change. But the latter represents also the total amount of heat that has ever been acquired – if, according to our assumption, the livening force (kinetic energy of thermal motion) contained in the body was not altered during the change of physical state.

Here we have just arrived at the most remarkable result of the mechanical theory of heat, which in words conveys the following facts: **If we know the amount of volume increase brought about by the heat-induced change of the physical state in a body, as well as the pressure to be used in overcoming the change in physical state at different temperatures, then the external work is completely determined, and hence the internal work as well as the amount of heat consumed during the change of physical state might also be calculated using Clausius’ law in a straightforward way** \(^7\).

\(^7\) The derivation of this result using the ordinary form of the Second Basic Law could be found in: Kirchhoff, Pogg. Ann. 108, p. 177.

Excerpt 13. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

The new part filled with the symbols ""]" ""]" ""]" the ""]"holes ""]" in the text.

Meanwhile, if we initially apply the above-considered law to permanent gases, then the reason for which the zero point of the absolute temperature scale should be set to the value of -273° C immediately follows. Indeed, according to our experience, if no internal forces resist the expansion of a gas; then the inner work is equal to 0, then for a small increase in volume, by which the pressure does not change markedly, it is in accordance with equation (13):

\[
J = \left( T \frac{\delta p}{\delta T} - p \right) \delta v = 0 , \tag{16}
\]

\[122\] i.e., it should come as follows:

\[
T \frac{\delta p}{\delta T} = p \tag{17}
\]

The gas expansion should be carried out at 0°. Then, if \( p \) stands for the initial pressure, the pressure at a temperature higher by about \( \frac{\delta T}{T} \) ought to be increased according to Mariotte’s law:
\[ \frac{\delta p}{\delta T} = p\alpha , \]  

where \( \alpha \) stands for the gas expansion coefficient. It is equal to 0.003665 or \((1/273)\). With this in mind we calculate:

\[ T\alpha = p , \]  

And thus \( T\alpha = 1 \), and, taking into account the value of \( \alpha \), \( T = 273 \), that is, the absolute temperature corresponding to 0°C lies at -273°C. Therefore, the zero point at -273°C is the zero of the absolute temperature scale.

Excerpt 14. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

4. E. Starikov statements

Now let’s see the opinions of E. Starikov… and meditate on them…

Coloring (yellow) some statements is due to F. Galetto

What are the most important and general points touched by Prof. Horstmann in his above communication? We have marked them by green colors and shall now summarize them as follows.

Every realistic natural process is possessed of the two main factors:

a) The Driving Force (or, as the ancient would tradition require, Vis Viva, in other words, the Livening Force);

b) The ubiquitous, omnipresent hindrances/obstacles/obstructions/hurdles/vaults/...etc.

Have we just communicated something exceptional? Not at all, the above statement is in fact trivial! But the real problem ought to be: how to correctly describe and analyze such situations – in terms of physics/chemistry/… etc. …?

By the way, there is a pertinent citation by The Great Helmsman, Mao Tse-tung, …. (NOT fully given here by F. Galetto!!! See the Appendix)

"What is a problem? A problem is the contradiction in a thing. Where one has an unresolved contradiction, there one has a problem. OMISSIS ‘’"

… With all this in mind, a good idea in our case would first of all be to use the Language of Energy (it would be handy to denote the latter: ‘Energetics’). Further, we have to ascribe some portion of energy to the Livening Force and another one to the Hurdles. The actual energetic balance would then determine the course of the process under study.

To energetically describe the Livening Force we use the suggestions by Herrn Gottfried Wilhelm Leibniz (1646 – 1716), … This is why we might readily accept that the Livening Force ought to be delivered by the Kinetic Energy. It is important to note here that the Livening Force cannot arise by itself from nothing, for there always ought to be the relevant prerequisites. The latter could be energetically analyzed in terms of the Potential Energy, in other words, the Energy Supply. If such a supply isn’t dwindling, it is in principle to somehow convert the Potential Energy to its Kinetic counterpart.

And now it’s just the time to revert to the results by Hon. Sir Isaac Newton, who wasn’t accepting the ideas of Gottfried Leibniz, but had built up the logical basis of the classical mechanics, so that we would now greatly appreciate applying Newton’s Third Basic Law, according to which “For every action, there is an equal and opposite reaction.” …
The latter point was/is/remains extremely important for any process evolving in time. Whatever the actual nature of the process in question there always ought to be two main energy contributions governing the course of the process, using our ‘energetic language’: The Kinetic Energy (Vis Viva), as well as some energy contribution from the omnipresent hurdles/obstacles/...& so on, so forth ... … And this is just what Nicolas Léonard Sadi Carnot was most probably intending to demonstrate us using his ingenious cyclic gadget … Then, the great contributions of Rudolf Clausius and Hon. William Thomson, 1st Baron Kelvin, was to stress that the energy contribution due to the obstacles ought to consist in the dissipation/devaluation of the so-called ‘useful energy’, that is, of the energy promoting the processes which are capable of carrying out some useful work.

The next step was to work out some valid methods of describing and properly analyzing the processes of interest, to have a relevant theory for the design of the relevant evices adequate to performing some useful work...

Here the works by Hermann Ludwig Ferdinand von Helmholtz and Gustav Robert Kirchhoff in Germany ought to be mentioned in the first line. Noteworthy, August Friedrich Horstmann was but the only colleague in Germany who was capable of preparing the correct of all the achievements in the thermodynamics of his time. Still, to our sincere regret, he had but no more time to continue his important work.

Excerpt 15. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

E. Starikov writes (last sentence of Excerpt 15)

Noteworthy, August Friedrich Horstmann was but the only colleague in Germany who was capable of preparing the correct of all the achievements in the thermodynamics of his time. Still, to our sincere regret, he had but no more time to continue his important work.

If F. Galetto is right in the previous pages then we should say … to our sincere regret, he had but no more time to correct his work.

Let’s consider now the set of statements

… we have to ascribe some portion of energy to the Livening Force and another one to the Hurdles.... OMISSIS...

Every realistic natural process is possessed of the two main factors:

a) The Driving Force (or, as the ancient would tradition require, Vis Viva, in other words, the Livening Force);

b) The ubiquitous, omnipresent hindrances/obstacles/obstructions/hurdles/vaults/...etc.

and the

...Newton’s Third Basic Law, according to which “For every action, there is an equal and opposite reaction.”

We prefer the following way of saying (Newton’s Third Law):

If two objects interact, the force \( \vec{F}_{12} \) exerted by object 1 on object 2 is equal in magnitude and opposite in direction to the force \( \vec{F}_{21} \).
Note that the **Newton's Third Law makes reference to FORCES ... NOT to energies.**

Is there any consequence of Newton's Third Law related to energy?

Let’s see...

To get the answer, let’s consider a **pendulum** (we did it also before...).

A small ball of mass $m$ is suspended from a string of length $l$, fixed at point $O$, as in figure 5. $\vartheta$ is the angle between the vertical line $OH'$ and the string $OP$, at time $t$; $\vartheta_0$ is the angle at time $t=0$; $h$ is the height $HH'$ of the ball centre from the ball minimum position $H'$.

**IF** at time $t=0$ the angle is $\vartheta_0=0$, **THEN** the pendulum is in its equilibrium position $H'$; the force acting on the ball $\vec{mg} = \vec{F}_g$ [Newton’s second law] is the gravitational force: it is counterbalanced by the stress $\vec{T}$ of the string [Newton's third law]. The pendulum is at rest and it will not move [Newton’s first law].

If we want that the pendulum moves we must provide the ball with either an impulse or a force; let’s assume that due to that (before time $t=0$) at time $t=0$ the initial angle is $\vartheta_0$; on the ball acts the force $m\vec{g} = \vec{F}_g$ (the vector $MP$); it can be “divided” into two vectors: $\vec{F}$ tangential to the trajectory of the ball and the other $\vec{F}'$ orthogonal to the trajectory; it is counterbalanced by the stress $\vec{T}'$ of the string [Newton’s third law]. The tangential force $\vec{F}$ causes the movement.

---

Figure 5. a pendulum

From Newton’s laws we can derive energetic quantities, at time $t$

- The potential energy $E_P = mgl(1 - \cos \vartheta)$
- And the kinetic energy $E_K = \frac{mv^2}{2}$

Due to the Conservation Energy Theorem we have

$$mgl(1 - \cos \vartheta_0) = E_P + E_K = mgl(1 - \cos \vartheta) + \frac{mv^2}{2}$$

from which we derive the ball speed

$$v = \sqrt{2gl(\cos \vartheta - \cos \vartheta_0)}$$

We notice that in the position $H'$ the energy is only kinetic (it has its maximum) while it is zero at the maximum distance with angle $\vartheta_0$: the energy is only potential (it has its maximum).
maximum).
This example show in a very simple way the Horstmann’s ideas:

It is important to note here that the Livening Force cannot arise by itself from nothing, for there always ought to be the relevant prerequisites. The latter could be energetically analyzed in terms of the Potential Energy, in other words, the Energy Supply. If such a supply isn’t dwindling, it is in principle to somehow convert the Potential Energy to its Kinetic counterpart.

In our example the Energy Supply is \( mgl(1-\cos \theta_0) \) …
BUT, for getting the Energy Supply we had to provide an impulse to the ball…
AND to provide an impulse to the ball (for getting the Energy Supply) we had to …
And so on...

"'there ain’t no such thing as a free lunch'"

After some time, depending of various factors (the stress-strain of the string, the air around the ball, …) the ball velocity go to 0: the pendulum rest on its equilibrium position. The energy is zero.
It a way of life!
Let’s consider another example.

When cars are propelled, the driving force for the motion is provided by the energy supplied by engine to the wheels that rotating the tires on the road generates a force which uses its counterpart the friction, the force exerted by the road on the car [Newton’s third law]. An impulse is applied to the car from the roadway, and the result is a change in the momentum of the car.

If we want to stop we act on the brakes and reduce to 0 the momentum of the car: we need the friction exerted by the road on the car.
SO friction by the road on the car is a very important factor for driving the car.
IF there were NO friction we could neither start, nor stop, with our car …
The friction generates waste but it is essential for our system.

If the car is moving on a flat, horizontal road and we need to follow a curve we make the turn safely only if the maximum speed the car is less than a certain limit, when pavement is dry; when pavement is wet we must slow down the speed if we want to turn safely.

In this car example the Energy Supply is the engine fuel…
BUT, for getting the Energy Supply someone had to transform the petrol to gasoline …
AND to find the petrol (for getting the Energy Supply) someone had to …
AND to originate the petrol the Nature had to …
And so on…

And now let’s consider the following case: an airplane flying towards East for some kilometers so that the flight could be considered horizontal.
Let \( M \) be its mass (including the mass \( m \) of the fuel) and \( \vec{v} \) its speed (constant) in the air [Newton’s second law of an object under the effect of forces that balance].

\[ M\vec{g} = \vec{F}_g \] [Newton’s second law] is the gravitational force (the attractive force exerted by the Earth on an object) [we assume that the mass is concentrated in the centre of mass of the airplane] causing the airplane falling down to the Earth; in order the airplane stays at 5000 m of altitude there must exist [Newton’s second law of an object under the effect of forces that balance] a vertical force preventing it to fall: it balances \( M\vec{g} \) and is named "aerodynamic lift" and it is provided by the wings.

Is this the “Driving Force”, mentioned in the point a)?
Absolutely not.
What in a) is named “Driving Force” (“Vis Viva”, “Livening Force”) is actually Kinetic Energy, NOT a force… It is said in Excerpt 15...

What are, in this case (airplane flying towards East), the ubiquitous, omnipresent
hindrances/obstacles/obstructions/hurdles/vaults/+...etc., mentioned in b)?

There are several factors, such as the mass of the airplane, the speed of the airplane, the area of the wings, the wings’ curvature, and the angle between the wings and the horizontal, the CX of the airplane, the air flow viscosity/resistance against flying, turbulent air flow...

The airplane engines (turbines) generate a horizontal force (towards East) by fuel consumption (and propulsion exhaust gases act towards West) [Newton’s Third Law and the law of conservation of linear momentum as applied to an isolated system, where the system is made of the engines their ejected propulsion exhaust gases (air and burnt fuel)]. Because the gases are given momentum when they are ejected out of the engines, the engines receive a compensating momentum in the opposite direction. Therefore, the airplane is accelerated as a result of the “push,” or thrust, from the exhaust gases. When flying the airplane receives an opposite force due to the air so that the center of mass of the system (engines plus expelled gases) moves uniformly; then the speed of the airplane is kept constant (let say; cruise speed) [Newton’s second law of an object under the effect of forces that balance]. The mass M (including the mass m of the fuel) is reduced by \( \Delta m \); the kinetic energy of the airplane (with engines exhaust gas) is kept constant (at the expense of chemical potential energy in the fuel).

Let’s consider figure 5, where the air approaching from the right is deflected downward by the wing; consider that the airstream approaches the wing horizontally from the right with a velocity (vector) \( \vec{v}_1 \); we see the streamlines flowing around an airplane wing. The tilt of the wing causes the airstream to be deflected downward with a velocity (vector) \( \vec{v}_2 \). Because the airstream is deflected by the wing, the wing must exert a force on the airstream. The curvature of the wing surfaces causes the pressure above the wing to be lower than that below the wing due to the Bernoulli effect. This pressure difference assists with the lift on the wing. According to Newton’s third law, the airstream deflected by the wing exerts an upward force \( \vec{F} \) on the wing from the air (this is equal in magnitude and opposite in direction to the force of the wing on the air). Force \( \vec{F} \) has a vertical component \( \vec{F}_1 \) the aerodynamic lift and a horizontal component \( \vec{F}_2 \) the drag, opposite the velocity of the wing, due to air resistance, there is also a force: drag.

![Figure 6. the wing section of an airplane, flying form West to East; flow of air and forces](image)

When landing the aircraft needs friction between the tires and the pavement (plus an inverted thrust of the engines) and brakes....

At last let’s consider a Formula 1 car in a Formula 1 RACE.

In this case the friction between the tires and the pavement is important; the air flow is important; the wings are important to have a force opposite to the lift of the airplane; ...

In these last two examples the Energy Supply is the engine fuel...

BUT, for getting the Energy Supply someone had to transform the petrol to gasoline ...
AND to find the petrol (for getting the Energy Supply) someone had to …
AND to originate the petrol the Nature had to …
And so on…
Moreover, we need the air flow (opposite to the aircraft movement) to get the lift that keeps the airplane flying…
Obviously things are quite different in the free space… BUT there we need gravitational forces, controlling accelerations (positive and negative), electromagnetic communications (forwards and backwards), …
Friction, air flow, gap (difference) of temperatures, forces, masses, gravitation, … are essential for getting the intended goal of the system i.e. what we want to do!

""there ain’t no such thing as a free lunch"

From all these cases it should be clear that the

...Newton’s Third Basic Law, according to which “For every action, there is an equal and opposite reaction.”

is NOT APPLICABLE to the “Driving Force”, mentioned in the point a).
It is APPLICABLE only to FORCES:

If two objects interact, the force \( \vec{F}_{12} \) exerted by object 1 on object 2 is equal in magnitude and opposite in direction to the force \( \vec{F}_{21} \) exerted by object 2 on object 1: \( \vec{F}_{12} = -\vec{F}_{21} \)

All that becomes clear using properly Mathematics.

5. Conclusion

Reader, do you think that above there was

5. 1. The correct formulation of the 2-nd Basic Law of thermodynamics
by Prof. Dr. August Friedrich Horstmann???

Reader, do you think that we can accept the following?

But if we adopt the standpoint of A. F. Horstmann, J. W. Gibbs, P. B. Freuchen, N. Engelbrektsson, K. A. Franzen, G. A. Linhart, M. B. Weinstein – and other colleagues from the ‘Rational’ branch – we shall have to take into account one very important point:

The absolute zero temperature can never be reachable **BECAUSE THE ENTROPY CAN NEVER COME TO ZERO**.

The entropy might MATHEMATICALLY come to zero, but NOT PHYSICALLY. The energetics teaches us that entropy corresponds to the WASTE, USELESS ENERGY. F. Simon, the apprentice of W. Nernst, was absolutely right, when exclaiming, that ‘it is impossible to deprive any system of its entropy’!

Excerpt 16. taken from a document of E. Starikov, downloaded from Research Gate (see Appendix)

We personally do not agree on some of the statements

The absolute zero temperature can never be reachable **BECAUSE THE ENTROPY CAN NEVER COME TO ZERO**.

The entropy might MATHEMATICALLY come to zero, but NOT PHYSICALLY.
We agree that PHYSICALLY the entropy cannot be ZERO. Then we agree that

... THE ENTROPY CAN NEVER COME TO ZERO.

As a matter of fact, all possible states of any system, at (absolute) temperature \( T=0 \) [not reachable!!!], have the same entropy. (see figure 7)
Hence, the same entropy of every system, at (absolute) temperature \( T=0 \), can be set MATHEMATICALLY equal to ZERO, BECAUSE we have always to deal with entropy differences \( \Delta S \).

Figure 7. Equations of state of a substance, undertaking isothermal and isentropic transformations for cooling it (e.g. adiabatic demagnetization, or two different pressures \( X_1 \) and \( X_2 \))

We agree, as well, that PHYSICALLY (see figure 7)

The absolute zero temperature can never be reachable ...

because it takes infinite time to get there (we can consider this as a way of stating the\(^3\) principle of Thermodynamics; it “quantifies” how long it takes to cool a system: we can say that it is impossible for any process to reduce the temperature of a system to its absolute minimum possible value in a finite number of physical operations). At absolute zero temperature the “thermal” motion should cease and the position of the molecules are fixed/certain in pure crystalline substance, defining the absolute zero entropy (the Third Principle of Thermodynamics). For not purely crystalline substance, the positions of the molecules are not uniquely determined and entropy is not exactly zero at absolute temperature (but some residual value).

But we DO NOT agree that

The absolute zero temperature can never be reachable BECAUSE THE ENTROPY CAN NEVER COME TO ZERO.

It is absurd, MATHEMATICALLY and PHYSICALLY, to derive that SINCE THE ENTROPY CAN NEVER COME TO ZERO

THEN the absolute zero temperature can never be reachable.

Since \( dS = d^*Q/T \), as \( T \to 0 \), we know (see figure 7) that \( d^*Q \to 0 \); therefore the ratio \( d^*Q/T \) can be such that \( S(T \to 0) \to \text{constant} = S_0 \), which could be also zero or \( >0 \) ... Since experimentally we find that \( C_V \to 0 \) as \( T \to 0 \) and we know that \( d^*Q = C_V dT \), with \( V = \text{constant} \), we get (\( S_0 \) is the integration constant)

\[
S(T) - S_0 = \int_0^T \frac{C_V(T)}{T} dT
\]

with \( S_0 \) which could be also zero or \( >0 \) ...
AGAIN [6, 7, 8], all that becomes clear using properly Mathematics.

The fact that entropy cannot become zero can be understood by thinking at the intimate structure of matter, as given by Quantum Mechanics (mentioned here in a very short way…).

We talked before of atoms and molecules (and their energy). Since $d^*Q$ is related to amount of kinetic energy transfer and $T$ is related to kinetic energy of the molecules (atoms) the ratio $d^*Q/T$ is given by the change of the number of molecules $n_i$ in the energy levels $E_i$.

Now we add that atoms (contrary to their name meaning indivisible) are made of several smaller interacting particles. In an atom there are a nucleus [made of nucleons (made of quarks)] and electrons. The interacting particles continuously emit and absorb field particles. The emission of a field particle by one particle and its absorption by another manifests itself as a force [nuclear force, strong force, weak force, electromagnetic force, gravitational force], between the two interacting particles (we know photons, gluons, W/Z bosons, and gravitons which are the mediators of the forces.). The same happens for more than two particles. All particles other than field particles are in two broad categories, hadrons (particles made of quarks) and leptons: quarks and leptons have spin ½ and hence are fermions, whereas the field particles have integral spin of 1 or higher and are bosons.

All these came out from the (so called) Big Bang... The evolution from very very high energy and very very high (cosmic) temperatures is proved by the “actual” thermal radiation associated with a temperature of 2.7 K (black body radiation at 2.7 K: if you know the radiation flux at any known frequency, that determines the temperature of the radiation field). The radiation we see today came from an era when the Universe was hot. When it had a temperature $T > 13$ev, protons, electrons and photons were the main constituents of a plasma in equilibrium; the expansion of the universe cooled the plasma to where hydrogen atoms formed (called the era of recombination, even though the atomic constituents had never been combined prior).

Absolute zero corresponds to the point at which atoms/molecules stop moving completely (i.e. stop having kinetic energy, due to the energy of collective lattice vibrations), which is why nothing can be colder.

That does not tell the whole story … However, at very low temperatures, close to absolute zero, the very few electrons that are excited above the Fermi level contribute to the internal energy and $C_V$ (and to entropy $d^*Q=C_VdT$) more than the energy of collective lattice vibrations.

Nevertheless, hadrons, leptons and field particles (with their force mediators) [as we know from experience and theory] cannot stop acting near absolute temperature, unless the matter, as we know it, disappear (no photons exchange, no neutrinos, no bosons exchange, no…)… Entropy is related to the number of accessible microstates, and for a system consisting of many particles (atoms/molecules), quantum mechanics indicates that there is only one unique state (the ground state) with minimum energy...

But QCD (Quantum Chromodynamics) tells us a different story...

Hence...

Some last comments.

I have to acknowledge that I do not share some of the fundamental ideas of E. Starikov about Thermodynamics (according to my understanding, hoping that I am right; if I am not, it depends on my poor ability to follow E. Starikov way of “teaching”; I beg pardon to E. Starikov and to the readers):
There are two kinds of Thermodynamics: the Conventional one and the TRUE ("Rational") one
There is only one Fundamental Law of Thermodynamics, NOT TWO laws
Any physical transformation is a "continuous" battle between Energy and Obstacles/Hindrances (the war will never stop); it is related to the Newton’s Third Basic Law, according to which “For every action, there is an equal and opposite reaction.”

Reader, please answer…

IF, in Thermodynamics, there is only one Fundamental Law and NOT TWO laws
THEN
why, in Mechanics, there are THREE fundamental laws and NOT only one?

Reader, please consider all the cases we showed before…

There are several Conservation Laws; two of them are
- The Energy Conservation Law, for any transformation (cycles included)
- The Entropy Conservation Law, for Reversible Cycles [ideal cycles]

Any physical cycle (transformation) is not ideal and the Entropy Conservation Law breaks down…

References
[1.] Starikov E., Chapter 5, The True Physical-Chemical Foundations of Thermodynamics: What Ought to be the Proper Mathematical Instrument? Downloaded from Research Gate on 20-09-2019
[3.] Galetto, F., 2019, Addendum to Mathematics of Thermodynamics. Academia.edu & HAL
[4.] Galetto, F., 2019, Entropy of Linhart_a nonsense_PREAMBLE. Academia.edu & HAL
[6.] Finzi B., 1359, Cosa è la temperatura (what is the temperature) Periodico di Matematiche, serie IV, vol. XIV and Academia.edu
APPENDIX (taken from a document of E. Starikov, downloaded from Research Gate)

Chapter 5 downloaded from E. STARIKOV on Research Gate 20-09-2019

The True Physical-Chemical Foundations of Thermodynamics: What Ought to be the Proper Mathematical Instrument?

5. 1. The correct formulation of the 2-nd Basic Law of thermodynamics

Prof. Dr. August Friedrich Horstmann

About the second law of thermodynamics and its application to some decomposition phenomena
(Annalen der Chemie und Pharmacie. VIII. Supplementary volume, pp. 112-133 1872)

“Certain decomposition phenomena studied in greater detail in the recent time allow for the unique application of the second law of thermodynamics, especially in cases where heat might decompose chemical compounds according to some consistent rules, in that the heat performs work against the natural trend called chemical affinity. It looks like, and it has already been often pointed out, that the doctrines summing up the theory of heat in the sentence of the latter type might also be of great interest to chemists.

Remarkably, physicists mostly know such trains of thoughts only. This ought to result [113] from the fairly abstract considerations of the main topics in the field – using rather restrictive mathematical tools till nowadays as well as from the absence of their really popular representation. Before considering the practical applications, I would greatly appreciate presenting a concise statement of the relevant results within the theory of heat, which might hopefully contribute to their popularization. With this in mind, my current presentation pretends to be neither original, nor rigorous; in effect, it should boil down to nothing more than just familiarizing the interested readership with the actual meaning of the relevant equations and the proper ways of using the known hypotheses.

1. On the one hand, heat can be transformed into work and, on the other hand, heat can be generated from motion. Hence, we conclude that heat is itself a movement, because movements themselves can be converted into work. The quantity of work, which the movement might in principle produce, is determined by the Vis Viva (Livening Force) of this movement – or, in other terms – by the kinetic energy of the movement, i.e., half the product of the squared velocity and the mass of the moving body. The same applies to the heat: A given quantity of heat corresponds to a certain amount of kinetic energy, which is, in turn, equal to the work to be produced from the mentioned quantity of heat. This is content of the first law of thermodynamics confirmed by the experience: Work and heat are equivalent.

2. Further, the experience teaches that not just any amount of heat can be implemented in work to the full extent, and the very fact, that in the caloric machine heat is always applied at a higher temperature, indicates that it is just the temperature that determines how much from a given amount of heat can be converted into work. We immediately rationalize the latter statement, if we take into account that while producing work out of heat the working body always expands under the influence of heat and has usually to overcome some resistant obstacles/hindrances/interferences/impediments (… etc.) during its expansion. The extent [114] of the latter effects is clearly dependent on the actual type of the working body employed, but all of these resistant obstacles are indeed the higher the applied temperature, which is in particular very clearly observable when choosing gases and vapors as the working bodies. Therefore, the work performable by the heat in such operations increases with the temperature; meanwhile, the law governing the latter increase can’t always be deduced from direct observations, because in general, we have to work not only against the ubiquitous external resisting factors (observable obstacles/hindrances/impediments, etc.), but also against various internal resisting forces (cohesion, affinity, and/or further snags), which are in principle expected, but might in fact be inaccessible to the conventional measurements. The following considerations should first clarify the nature of the law in question; and we shall then use the same train of thoughts to draw our conclusions on the amount of work to be performed against the mentioned snags (i.e., resisting internal forces).

3. Temperature of a body is the measure of the actual amount of heat present in this body, i.e., of the entire livening force/kinetic energy of the thermal motion. Importantly, at the zero points of the ordinary thermometric scales the body still ought to contain heat. Thus, in the following we shall speak only of the so-called absolute temperature, with the initial point of this scale being the one in which all the thermal motion really ceases. This zero point of the absolute temperature scale is in effect equal to -273°C, according to an assumption we shall consider in more detail later. Then, the entire livening force/kinetic energy of the thermal motion should be essentially proportional to the absolute temperature.

4. If we imagine that the thermal motion is in effect carried out by the smallest particles of the body under study, the livening force/mean kinetic energy of such particle motions should then also be proportional to the temperature; Thus, the particles move with certain speeds determined by the temperature, in following certain [115] trajectories dependent
on the actual physical state of the other body. For example, the trajectories of the oxygen and hydrogen atoms will be exhibiting different designs, if they are pertinent to solid, liquid or gaseous water or just to a gas mixture of chemically unbound oxygen and hydrogen. As a consequence, the different physical-chemical properties exhibited by the same chemical substance in these various physical-chemical/aggregate states are due to the different shapes of the trajectories in question; conversely, the shape of the atomic trajectories ought to fully reflect the manner in which the atoms are chemically bonded, and thus determine what is the actual physical state of the body to which they belong, but not the speed of these atoms.

5. With this in mind, the unanswered question still remaining is about the interrelationship among the average speeds of different atoms in the various physical-chemical states, but at one and the same temperature; or, in other words, whether the amount of heat present in the body is dependent not only on the temperature, but also on the physical-chemical state of the body in question. That the latter dependence is not the case should certainly be the simplest and the most plausible assumption in this respect; indeed, if we bring different systems containing hydrogen and oxygen in their various physical-chemical states, e.g., as a water vapor and as a gas mixture without chemical bonding, into contact with each other at the same temperature then there will be no change of the total temperature. The average livening force/kinetic energy of all the atoms involved will also not change as a result, for it was already the same before the contact. Such an assumption is also in pretty good accordance with some earlier observations on the specific heat of gases – the fact only to be noted here\(^*\).

\(^*\) See on this subject: Clausius, Abhandlungen I, 266 ff. as well as my own remarks, Berichte der Deutschen Chemischen Gesellschaft II, 723 ff.

Therefore, we might safely assume, that the average livening force/kinetic energy of the atoms and, consequently, their average speed \(^{[116]}\) is dependent on the temperature only and never on the shape of the trajectories followed by the atoms during their movements.

6. Still, the velocities of the atoms ought to be in a certain relationship with the forces exerted on them, which is of importance for our present purposes. The forces partly resulting from the inter-atomic interactions, partly from some external influences, should then determine the shape of the trajectories corresponding to the given physical state. The actual nature of these forces, as well as the shape of the resulting trajectories, are practically unknown to us, but, as to the amount of the forces involved, we might nonetheless plausibly assume that at any given moment of the time and at any point of a particular atomic trajectory they ought to boil down to the centrifugal force generated by the movement, for otherwise the atom would just have to leave its actual trajectory. Then, for a circular movement the centrifugal force is

\[
\frac{mv^2}{R}, \text{ where } m \text{ stands for the mass, } v \text{ – for the velocity of the atom and } R \text{ – for the radius of our imaginary circle.}
\]

The atomic trajectories are in reality not necessarily circular; but whatever the actual shape they could acquire, we might always take the actual atomic orbit into such small sections that each of the latter in its entire length might be coincident with a circle (called the curvature circle), whose radius is equal to \(r\). Then, at this particular point of the trajectory, the centrifugal force is \(\frac{mv^2}{r}\). If the velocity of the atom gets greater due to the increase in temperature, e.g., it’s now about \(v_2 > v\), then so does the centrifugal force, and – therefore – all the other forces ought to grow as well, if they still have to hold the atom within its actual orbit. If we denote such forces by \(k\) and \(k_1\), we arrive at the following expressions:

\[
k = \frac{mv^2}{r}, \quad \text{and} \quad k_1 = \frac{mv_1^2}{r};
\]

or

\[
k = \frac{mv^2}{r}, \quad \text{and} \quad k_1 = \frac{mv_1^2}{r}; \tag{1}
\]

And finally we get:

\[
k = \frac{mv^2}{r}, \quad \text{and} \quad k_1 = \frac{mv_1^2}{r}; \tag{2}
\]

\(^{[117]}\) that is, the interrelationship among such forces ought to safely mimic the one among the actual livening forces/kinetic energies of the atoms. This applies to each atom at each point of its trajectory. Since only the average livening force/kinetic energy of the atoms should be proportional to the temperature, we should also conclude that the actual inter-atomic forces must increase in proportion to the temperature as well.

7. Summing up all the above, we stress that the temperature increase ought to trigger the change of physical state, whereas the atoms ought to leave their previous orbits, if there would be no simultaneous increase in the resistant factors/forces tending to preserve the atoms in their current trajectories. And, as soon as the resistance in question stems from the inter-atomic forces only, there is no way to change anything. Still, according to the experience in many cases, the external pressure supports the internal forces holding together the atoms in the system in their resistance against the heat-induced forces driving the atoms apart from each other, and the magnitude of the external pressure might be arbitrarily variable. The latter fact, e.g., allows preventing the evaporation of liquids by increasing the external pressure despite an elevated temperature. And, as the experiments triggered the present communication clearly show, the same holds for heat-induced desorption of absorbed gases, escape of the crystalline water, decomposition of chalk and of the ammonium-chloride compounds, etc. It is for the present all the same, how exactly the external
pressure acts on the orbits of individual atoms; but, if the latter effect takes place and if it is possible to prevent a change of physical state by increasing the external pressure along the temperature growth, then we know from the foregoing that the pressure-induced resistance to this particular change of physical state must anyway grow in the same proportion as the temperature.

8. Any change of state [118] preventable by external pressure might be arbitrarily observable at various temperatures, but one solely has to let the pressure be so high that the resistance to the heat-induced change of the physical state might still be overcome at this particular temperature.

With all this in mind, the work to be performed in the latter case is definitely growing along with the resistance; because the other factor, namely the way, which the atoms have to lay back, remains just the same.

Then, it follows from what we know about the resistance that the whole amount of work done by the heat at any change of the body’s physical state ought to be proportional to absolute temperature at which this particular change occurs.

And this is just the law we are seeking for, which must anyway be carrying the name of Clausius\(^*\), who was undoubtedly pioneering its actual formulation.

\(^*\) It should be mentioned here, how to formally get to the law by Rudolf Clausius starting from the ordinary form of the Second Basic Law of thermodynamics. The analytical expression of the latter conveys that for a reversible cyclical process the following is true: \(\frac{dQ}{dT} = 0\); Then, the quantity of heat supplied to the body ought to be a function of two variables, one of which is the absolute temperature (\(T\)) itself, and the other (\(x\)), which should determine the form of the atomic paths. It is then possible to write \(dQ = Xdx + CD\) and to satisfy the latter equation according to the rules of differential calculus. We get the following expression as a result:

\[
\frac{d}{dT} \left( \frac{X}{T} \right) = \frac{d}{dx} \left( \frac{C}{T} \right);
\]

or after consequently performing the operation of differentiation:

\[
T \frac{dX}{dT} - X = T \frac{dC}{dx};
\]

The above equation should, among other things, take into account that the following statements are simultaneously true:

\[
T \frac{dX}{dT} - X = 0; \quad \text{and} \quad T \frac{dC}{dx} = 0.
\]

The second of the expressions (5) corresponds to the condition given by us – namely that the amount of heat actually existing in the body [119] is not dependent on the atomic/molecular arrangement, while the first of the expressions (5) gives by integration \(X = T \text{ Const}\), which is nothing more and nothing less than just the Clausius’ law, because \(X\) is the amount of heat transformed into the work during the change of \(x\) to \(dx\). (See e.g. Clausius, Abhandlungen I, 264). This is exactly the context I have pointed out on another occasion (Berichte der Deutschen chemischen Gesellschaft, II, 726).

9. To express [119] the law in an equation, let us assume that the total work to ensure a particular change of the physical-chemical state (e.g., the evaporation of a quantity of water) at the temperature \(T\) is equal to \(W\), so that \(\Delta W\) would be the increase in this work when the temperature increases up to \(T + \Delta T\). Then, according to the law under study, we get:

\[
\frac{W}{W + \Delta W} = \frac{T}{T + \Delta T} \quad \text{oder:} \quad W = T \frac{\partial W}{\partial T}. \tag{6}
\]

Meanwhile, the total work \(W\) ought to consist of two parts, which might be viewed separately. The amount of work against internal forces is, say, \(J\), and its amount isn’t known to us for the present, but it is plausible to assume that such a work amount should be conserved for one and the same change of the physical state at different temperatures; Indeed, the way/trajectories the atoms have to cover/follow remain the same, and the internal forces are not temperature-dependent, if the spacing between the atoms remains the same. Strictly speaking, the forces under study might surely change in effect, because it’s not possible to completely prevent any inter-atomic arrangement alteration by applying the external pressure, but it is nonetheless possible to arrange for the temperature change \(\Delta T\) to be always so small that the inner work remains noticeably the same. The increase in the total work might then arise solely out of the increase in the external work. Bearing this in mind, we denote here \(E\) to be the work against the external pressure, so that \(\Delta E\) would then be its increase resulting from the temperature increase \(\Delta T\) – and finally we get:

\[
W = E + J \quad \text{and:} \quad \Delta W = \Delta E. \tag{7}
\]

As a result, the equation (2) in (6) [120] turns into:
10. From now on we shall deal with such changes of physical state that are accompanied by some gas formation. Let us then imagine some body enclosed in a cylinder with a movable punch, so that the external pressure should be brought about by some weights placed on the upper surface of this punch. In generating the external pressure to be just overcome at the temperature \( T \), we have to charge the punch with \( p \) units of weight; hence, if the upper surface of the punch is equal to \( f \), then an increase of the gas volume inside the cylinder would lift the weight \( pf \) to a certain height \( h \). Therefore, the external work to perform the latter movement could be cast as follows:

\[
E = pfh = p\delta v ,
\]

(9)

where \( \delta v \) stands for the increase in volume during the change of the physical state. If we denote \( p + \Delta p \) the external pressure corresponding to the temperature \( T + \Delta T \), then we arrive at the following statement:

\[
E + \Delta E = (p + \Delta p)\delta v ,
\]

(10)

And consequently:

\[
\Delta E = \Delta p \cdot \delta v ,
\]

(11)

11. Using the above results for \( E \) and \( \Delta E \) the equation (8) might be recast as follows:

\[
W = p\delta v + J = T \frac{\Delta p}{\Delta T} \delta v .
\]

(12)

And for the inner work we therefore get:

\[
J = \left( T \frac{\Delta p}{\Delta T} - p \right) \delta v .
\]

(13)

Finally, to mathematically formulate the equation under study in entirely strict manner we have to replace the expression \( \frac{\Delta p}{\Delta T} \) by the true derivative of the pressure \( p \) at the temperature \( T \), that is, by \( \frac{dp}{dT} \) – because, as already noted, the smaller \( \Delta T \), the exacter would be the equation for the infinitely small temperature changes.

Remarkably, any measurement of the inner work could be possible solely via determining the amount of heat spent for carrying out the work of interest, and therefore we have to bring the equations just derived into a usable form by multiplying them with the caloric equivalent of work = \( A \). Thus, we obtain as a result:

\[
Q = AT \frac{\Delta p}{\Delta T} \delta v .
\]

(14)

\[
Q_J = A\left( T \frac{\Delta p}{\Delta T} - p \right) \delta v .
\]

(15)

\( Q \) stands here for the amount of heat to be transformed into work during the physical state change. But the latter represents also the total amount of heat that has ever been acquired – if, according to our assumption, the livening force (kinetic energy of thermal motion) contained in the body was not altered during the change of physical state.

Here we have just arrived at the most remarkable result of the mechanical theory of heat, which in words conveys the following facts: If we know the amount of volume increase brought about by the heat-induced change of the physical state in a body, as well as the pressure to be used in overcoming the change in physical state at different temperatures, then the external work is completely determined, and hence the internal work as well as the amount of heat consumed during the change of physical state might also be calculated using Clausius’ law in a straightforward way.*

*) The derivation of this result using the ordinary form of the Second Basic Law could be found in: Kirchhoff, Pogg. Ann. 108, p. 177.

12. Meanwhile, if we initially apply the above-considered law to permanent gases, then the reason for which the zero point of the absolute temperature scale should be set to the value of -273° C immediately follows. Indeed, according to our experience, if no internal forces resist the expansion of a gas; then the inner work is equal to 0, then for a small increase in volume, by which the pressure does not change markedly, it is in accordance with equation (13):

\[
J = \left( T \frac{\Delta p}{\Delta T} - p \right) \delta v = 0 ,
\]

(16)

[122] i.e., it should come as follows:

\[
T \frac{\Delta p}{\Delta T} = p
\]

(17)

The gas expansion should be carried out at 0°. Then, if \( p \) stands for the initial pressure, the pressure at a temperature higher by about \( \Delta T \) ought to be increased according to Mariotte’s law:
\[ \frac{\delta p}{\delta T} = p\alpha, \quad (18) \]
where \( \alpha \) stands for the gas expansion coefficient. It is equal to 0.003665 or \((1/273)\). With this in mind we calculate:

\[ T\alpha = p. \quad (19) \]
And thus \( T\alpha = 1 \), and, taking into account the value of \( \alpha \), \( T = 273 \), that is, the absolute temperature corresponding to \( 0^\circ \) lies at -273°C. Therefore, the zero point at -273°C is the zero of the absolute temperature scale.”

**The further deliberations in this paper by Prof. Dr. A. F. Horstmann are** dealing with the particular applications of the above-sketched thermodynamic theory to different physical-chemical phenomena and detailed numerical work of crucial interest for physical chemists.

**What are the most important and general points touched by Prof. Horstmann in his above communication?** We have marked them by green colors and shall now summarize them as follows.

1. Every realistic natural process is possessed of the two main factors:
   a) The Driving Force (or, as the ancient would tradition require, Vis Viva, in other words, the Livening Force);
   b) The ubiquitous, omnipresent hindrances/obstacles/obstructions/hurdles/vaults/…etc.

   **Have we just communicated something exceptional?** Not at all, the above statement is in fact trivial! But the real problem ought to be: how to correctly describe and analyze such situations – in terms of physics/chemistry/… etc. …?

   By the way, there is a pertinent citation by The Great Helmsman, Mao Tse-tung, if we get rid of the conventional political husk around his name [The following citation is according to ‘Selected Works of Mao Tse-tung’, Volume 3, 1965, pp. 61-62]:

   **What is a problem?** A problem is the contradiction in a thing. Where one has an unresolved contradiction, there one has a problem. Since there is a problem, you have to be for one side and against the other, and you have to pose the problem. To pose the problem, you must first make a preliminary investigation and study of the two basic aspects of the problem or contradiction before you can understand the nature of the contradiction. This is the process of discovering the problem. Preliminary investigation and study can discover the problem, can pose the problem, but cannot as yet solve it. In order to solve the problem it is necessary to make a systematic and thorough investigation and study. This is the process of analysis. In posing the problem too, analysis is needed; otherwise, faced with a chaotic and bewildering mass of phenomena, you will not be able to discern where the problem or contradiction lies. But here, by the process of analysis we mean a process of systematic and thorough analysis. It often happens that although a problem has been posed it cannot be solved because the internal relations of things have not yet been revealed, because this process of systematic and thorough analysis has not yet been carried out; consequently we still cannot see the contours of the problem clearly, cannot make a synthesis and so cannot solve the problem well. If an article or speech is important and meant to give guidance, it ought to pose a particular problem, then analyze it and then make a synthesis pointing to the nature of the problem and providing the method for solving it; in all this, formalist methods are useless.”

   … With all this in mind, a good idea in our case would first of all be to use the Language of Energy (it would be handy to denote the latter: ‘Energetics’). Further, we have to ascribe some portion of energy to the Livening Force and another one to the Hurdles. The actual energetic balance would then determine the course of the process under study.

   To energetically describe the Livening Force we use the suggestions by Herrn Gottfried Wilhelm Leibniz (1646 – 1716), as duly analyzed and proven in detail by Mme Gabrielle Emilie Le Tonneller de Breteuil, Marquise du Châtelet-Laumont (1706 – 1749). This is why we might readily accept that the Livening Force ought to be delivered by the Kinetic Energy. It is important to note here that the Livening Force cannot arise by itself from nothing, for there always ought to be the relevant prerequisites. The latter could be energetically analyzed in terms of the Potential Energy, in other words, the Energy Supply. If such a supply isn’t dwindling, it is in principle to somehow convert the Potential Energy to its Kinetic counterpart.

   And now it’s just the time to revert to the results by Hon. Sir Isaac Newton, who wasn’t accepting the ideas of Gottfried Leibniz, but had built up the logical basis of the classical mechanics, so that we would now greatly appreciate applying **Newton’s Third Basic Law**, according to which “For every action, there is an equal and opposite reaction.”

   …

   The latter point was/is/remains extremely important for any process evolving in time. Whatever the actual nature of the process in question there always ought to be two main energy contributions governing the course of the process, using our ‘energetic language’: The Kinetic Energy (Vis Viva), as well as some energy contribution from the omnipresent hurdles/obstacles/…& so on, so forth …

   … And this is just what Nicolas Léonard Sadi **Carnot was most probably intending to demonstrate us using his ingenious cyclic gadget** … Then, the great contributions of Rudolf Clausius and Hon. William Thomson, 1st Baron Kelvin, was to stress that the energy contribution due to the obstacles ought to consist in the dissipation/devaluation of the so-called ‘useful energy’, that is, of the energy promoting the processes which are capable of carrying out some useful work.

   The next step was to work out some valid methods of describing and properly analyzing the processes of interest, to have a relevant theory for the design of the relevant evices adequate to performing some useful work …

   Here the works by Hermann Ludwig Ferdinand von Helmholtz and Gustav Robert Kirchhoff in Germany
Gibbs Free
1873', Oxford University Press, Oxford, apologetically… Thus, the apparently blind be put as follows: these both aren’t any more just the state variables, but are instead the state parameters to be voluntarily apologetic. Transactions of the unique Still, to avoid such a sad outcome, one has to add a couple 2003. With reference to the Gibbs free energy, we add the qualification that it is the energy free for non-conclusions reflecting the conventional terminological hotchpotch: [P. Perrot (1965): 'Methods of Thermodynamics', Cambridge University Press, Cambridge, Great Britain]."

Sure, to neophyte’s ears this ought to sound like a description of some special particular case: Indeed, the constant pressure and temperature are absolutely essentially defining some unique static, i.e., unsurmountable situation … So, here ought to stop any further consideration. Still, to avoid such a sad outcome, one has to add a couple of important words to this end, to break the logical cage to be inevitably formed after reading the above deliberations: It is throughout possible to control the both mentioned parameters of state from outside!

And this way, it is possible to voluntarily choose both the actual temperature value and the actual pressure value, so that these both aren’t any more just the state variables, but are instead the state parameters to be voluntarily set … The crucial difference here is that the variables could be changed by some external/internal reasons beyond the researchers control, whereas we are capable of voluntarily changing the state parameters … Thus, the apparently blind alley turns out to in fact be a true esplanade/mall, for what is changeable in principle should anyway be changing, whatever the driving force for the change of interest.

The latter interpretation seems to lie in parallel with what Prof. Gibbs was thinking about when speaking of the ‘available energy’. In effect the latter is nothing more and nothing less than [J. W. Gibbs (1873): A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces. Transactions of the Connecticut Academy of Arts and Sciences 2, Dec. 1873, pp. 382-404 (quotation on p. 400):]

"The greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition."

Remarkably, it is just in parallel to Prof. Dr. Gibbs that Prof. Dr. von Helmholtz was also working on some valid description of the quite general situation described by the above Gibbs’ citation. Meanwhile, his work boils down to the following apologetic conclusions reflecting the conventional terminological hotchpotch:

"In 1882, the German physicist and physiologist Hermann von Helmholtz coined the phrase ‘free energy’ for the expression $E - TS$, (where $E$ stands for the internal energy, $T$ – the temperature, $S$ – the entropy) in which the change in $F$ (or $G$) determines the amount of energy ‘free’ for work under the given conditions [R. Baierlein (2003): ‘Thermal Physics’, Cambridge University Press, Cambridge, Great Britain].

Thus, in traditional use, the term ‘free’ was attached to Gibbs free energy, i.e., for systems at constant pressure and temperature, or to Helmholtz free energy, i.e., for systems at constant volume and temperature, to mean ‘available in the form of useful work’ [P. Perrot (1998): ‘A to Z of Thermodynamics’, Oxford University Press, Oxford, Great Britain]. With reference to the Gibbs free energy, we add the qualification that it is the energy free for non-volume work [Howard Reiss (1965): ‘Methods of Thermodynamics’, Dover Publications, USA].”

… Why we consider the above citations to be apologetic will be clarified later on in the chapter. But first of all, we remain with a feeling that the Helmholtz’ result is nothing more than just another special particular case (now, for the constant values of temperature and volume), essentially like the result by Gibbs.

Meanwhile, from any serious textbook on thermodynamics we learn that ‘there is an intrinsic interconnection between the Helmholtz’ function and the statistical-mechanical partition function’, with the latter bearing the well-recognized universal physical sense, and immediately come across the pertinent well-known mathematical formula …
The questions immediately arise: Are the results of Gibbs and Helmholtz just two parts of one coin, or two rather different particular cases? ... Are we getting to some blind alley again?

On the other hand, the engineering thermodynamics introduces some fine difference between 'flow' and 'non-flow' processes, so that the former ones occur in the systems having open boundary and thus permitting mass interaction across the system boundary, whereas the latter are the ones in which there is no mass interaction across the system boundaries during the occurrence of process (see, for example, [Haywood (1974): Journal of Mechanical Engineering Science, v. 16, pp. 160-173, pp. 258-267] and the references therein).

Even using such a classification there is a need for both the Helmholtz and Gibbs functions, on the condition that these both are different expressions for the 'energy availability' or 'exergy' – just in the sense both Helmholtz and Gibbs were investigating the problem... All this but makes one to assume that there ought to be some essential, intrinsic interrelationship between the both. ... Is it really so?

To try answering the above question, let us just consider attentively and in detail the conventional equations of thermodynamics.

Is this idea completely new? Surely, not at all...

Nonetheless, we know only one publication, namely the small book by a physical chemist Dr. Robert Pauli, who could express a valid criticism of the then standpoints, as well as clearly formulate the problem to be solved – although there were really lots of colleagues all around the world, who was in the time of XIX-to-XX centuries actively working and publishing on the theme...


Remarkably, this work was accepted with a clear protest – both in Germany and in the USA:


To our mind, such a community’s reaction could be explained by a striking dissonance between the over-all, ubiquitous emotional atmosphere of that time we have already mentioned and the clear-cut suggestions of Dr. Pauli’s book, which in effect consisted in the appeal to attentively, thoroughly reconsider the two basic equations of thermodynamics – and Dr. Pauli had presented some starting points of such a re-consideration.

But, to our sincere regret, Dr. Pauli’s work could find no continuation... Why? This poser is difficult, for Dr. Robert Pauli had really disappeared in the unknown direction – thus, the only known information about him ought to be that he stemmed from a wealthy Jewish family in Berlin, being a son of an outstanding chemical engineer, Dr. Ph. Pauli, a director of the chemical factory ‘Meister, Lucius and Brüning’, presently well known as the 'Höchst AG'. Being thus a hereditary chemist, Robert Pauli had graduated the Leipzig University and gotten his PhD in chemistry under the academic leadership of Prof. Dr. Wilhelm Ostwald.

Sure, it is just under the influence of such an outstanding colleague that Dr. Pauli could be lively interested in the problems of thermodynamics. According to his own statements in the preface to his book, he devoted several years to attentively study the problems...

Still, he hadn’t joined the academic world, but became a successful chemical engineer (at the time of his book’s publication he was working at the electrolytic department of the 'Deutsche Solvay Werke' in Magdeburg), who could duly patent his achievements ... His further life could only be monitored from the following publications in the USA media: OMISSIS...