Starikov, 2:2
http://dx.doi.org/10.4172/scientificreports.624

Open Access
Scientific Reports

Open Access Scientific Reports

Review Article Open Access

Entropy-Enthalpy Compensation and Its Significance in Particular for Nanoscale Events

E B Starikov[1,2]*

[1]Institute for Theoretical Solid-State Physics, University of Karlsruhe, D-76128 Karlsruhe, Germany
[2]Department of Physical Chemistry, Chalmers University of Technology, SE-41296 Gothenburg, Sweden

Abstract

The basic thermodynamics behind the well-known, up to now hotly debated, notion of entropy-enthalpy compensation (EEC) is analyzed here in detail. Namely, any valid EEC phenomenon is considered using Carnot-cycle-type model, in which micro-phase transitions (MPTs) play a crucial role. Such MPTs could typically be some cooperative processes in (supra) molecular aggregates. Thus, the MPT notion ought to help rationalize the occurrence of the EEC in connection with the pertinent microscopic mechanisms.

Keywords: Entropy-Enthalpy; Conventional thermodynamics

Introduction

If we just try to look for the internet information about the "entropy-enthalpy compensation" (EEC), we'll come inter alia upon the Wikipedia paper on the theme [1]. After the short introduction, it is divided into two parts: "Causes" and "Criticisms".

The introduction of the Wikipedia paper in question is immediately connecting the EEC phenomenon to the Gibbs' free energy change, and directs the interested reader to the Pub Med's paper citation depository on the topic, which presently contains 121 citations… And then, also to the Purdue University's site about the Gibbs' free energy, as well as to the Frank L. Lambert's site about the true, intrinsic interrelationship between the latter and entropy. The Lambert's site presents a nice and insightful Q-and-A discussion between a student and a professor, directing the readership to the book "Entropy Analysis" by Norman C. Craig, as well as to three interesting 'Journal of Chemical Education' papers [2-4], dwelling on the relationship between the Gibbs' free energy and entropy, and also on the meaning of the entropy notion, but they don't contain any discussion about the EEC phenomenon.

The following chapter, "Causes", introduces two basic types of the EEC: the 'weak' and the 'strong' one–and stresses the statistical-mechanical meaning of the former one, whereas the last chapter, "Criticisms", is focusing the reader's attention on the paper by Cornish-Bowden [5], while the latter work is really radical, it is, by and large, not eradicative. As a consequence, the interested non-specialist readership ought to draw a conclusion that "the EEC is a phantom phenomenon", the opinion which is, by the way, rather widespread among the colleagues in the field as well. The truly thorough critical papers about the EEC are presented by Liu and Guo [6], and Cooper et al. [7], well, yes, in effect, an unskillful processing of equilibrium-thermodynamic, and/or kinetic experimental data might produce the "phantom EEC findings", but there is still definitely much-much more to the story!

The purpose of the present article is to try showing in detail, how thermodynamic concepts are involved into the physically-chemically valid EEC findings. We would, by the way, also like to touch here the still hotly debatable theme–what is the true, real meaning of the entropy notion–this is intrinsically connected to the meaning of the EEC phenomenon.

Is EEC connected to the conventional thermodynamics?

Mathematically, the general case of EEC can be expressed as a linear regression of enthalpy H on entropy S, that is,

$$H = T_c S + a \qquad (1)$$

where T_c stands for the so-called "compensation temperature", and the constant a has energy dimension.

In our work done by Starikov and Nordén [8], we have proven a theorem, which states that a "valid, non-trivial EEC is a necessary and sufficient condition for the existence of a hidden thermodynamical cycle". Besides, Equation 1 can also be very easily derived if we start considering some arbitrary smooth thermodynamic cycle and decompose it into a number of infinitesimal Carnot cycles, as suggested in the book by Müller and Weiss [9]. Then, for each infinitesimal cycle we may write as follows, assuming that the processes under consideration are slow enough and reversible:

$$dS = \frac{\delta Q}{T}; \quad dU = \delta Q - pdV, \qquad (2)$$

where the first equation is the Clausius definition of entropy, the second equation just expresses the 1st law of thermodynamics, Q stands for heat, U–for internal energy, p–for pressure, V–for volume and δQ means the inexact (path-dependent) differential, as opposed to the exact (path-independent) differential, d. And, after eliminating the inexact differential from Equation 2, we get:

$$dU = TdS - pdV, \qquad (3)$$

Which is nothing more than the conventional (Clausius-) Gibbs equation? Integrating the latter, provided that we are dealing with the isobaric-isothermal situation (p=const and T=const), and bearing in mind that H=U+pV by definition, would immediately lead to Equation 1. Indeed, assuming the isobaric-isothermal situation, we arrange physically-chemically that both p and T are in effect externally controllable parameters, so that, mathematically seen, the true integration variable coming to mind first of all would now be the system's volume–V. Hence, after the pertinent indefinite integration of Equation 3, we arrive at the following anti-derivatives' relationship:

$$U(V,\ldots) - U_{const} = TS(V,\ldots) - TS_{const} - pV(\ldots), \qquad (4a)$$

$$U(V,\ldots) + pV(\ldots) = TS(V,\ldots) - TS_{const} + U_{const}, \qquad (4b)$$

***Corresponding author:** E. B. Starikov, Institute for Theoretical Solid-State Physics, University of Karlsruhe, D-76128 Karlsruhe, Germany, E-mail: starikow@tfp.uni-karlsruhe.de

Received December 26, 2012; **Published** January 18, 2013

Citation: Starikov EB (2013) Entropy-Enthalpy Compensation and Its Significance in Particular for Nanoscale Events. 2: 624 doi:10.4172/scientificreports.624

Citation: Starikov EB (2013) Entropy-Enthalpy Compensation and Its Significance in Particular for Nanoscale Events. 2: 624 doi:10.4172/scientificreports.624

Where, by comparing Equation 4b with Equation 1, we get: $a \equiv U_{const} - TS_{const}$ and $T \equiv T_c$, so that the physical-chemical sense of the "constant as with the energy dimension" in Equation 1 is definitely nothing more than just the value of the system's Helmholtz free energy at the "compensation temperature" (and the corresponding system's volume).

Interestingly, Equation 4 are in accordance with the well-known fact that the entropy ought to be always defined up to an additive constant–this is immediately following from the fact that the entropy is proportional to the logarithm of the probability (the Boltzmann-Planck ingenious guess), as E. Fermi had mathematically-rigorously shown in his book [10]. Along with this, E. Fermi distinctly stated there: "*Of course, it should be clearly understood that this constitutes no proof of the Boltzmann equation, since we have not demonstrated that a functional relationship between entropy and probability exists, but have merely made it appear plausible.*"

In other words, we see that the "universal competition between energy and entropy" persuasively demonstrated in the book [9] clearly manifests itself as the EEC, at least in some particular isobaric-isothermal cases. For our present EEC topic, it is but of immense significance at least to try clarifying the interesting and important point: "What is then the entropy"? The latter, but still appears to be a hotly debatable issue.

In this connection, we would first of all like to mention the most recent series of books by Ben-Naim [11-14] on the theme. These books present clearly readable, instructive and witty deliberations of their author, who is a well-recognized specialist in the field, about what ought to be the real sense of the ENTROPY–one of the "most mysterious physical concepts" altogether. After persuasively showing that there is really no place for all of the "older" and "modern" views of entropy as "randomness", "disorder", "accessibility", "spreading", "freedom", etc., the author asserts the following claim:

"… We introduced the quantity referred to as the Shannon measure of information (SMI). We discussed this quantity, its properties, and its interpretations without any reference to thermodynamics. We mentioned that Shannon himself renamed his quantity "entropy", and many scientists still refer to SMI as the entropy. This practice is unfortunate and should be avoided … Starting from the SMI and applying it to the distribution of locations and moment (*my addition: of the ensemble of gas atoms*), we shall obtain entropy of an ideal gas as a particular case of SMI".

So, what all this boils down to for us, the readership? Well, it is clear that the SMI isn't identical to the thermodynamic entropy, but its mathematical appearance could be used to mathematically formally arrive at the expression for the latter. According to Shannon and Weaver [15], the SMI could be cast as follows:

$$SMI \equiv -K \sum p_i \log p_i \,, \tag{5a}$$

where p_i, i=1, …, N, are probabilities of some discrete random events and K stands for some proper constant, or if the random events under study are one-dimensional and obey the continuous distribution with the corresponding density function $f(x)$, $x \in [-\infty, \infty]$, then the SMI (for an information channel without memory) could be recast as follows [16], and the detailed discussion therein, where a propos, the SMI described by Equation 5, the author just dubs without more ado–"entropy":

$$SMI \equiv -K \int_{-\infty}^{\infty} f(x) \log f(x)\, dx \tag{5b}$$

Therefore, we, the readership, ought to draw the conclusion that … the SMI isn't just identical to the thermodynamic entropy, but the corresponding mathematical apparatus could in principle be used to formally derive the expressions for the latter. So that, yes, the functional interrelationship between the thermodynamic entropy and the probability is definitely plausible, but … how could we formally prove this? Would it be possible at all?

The answer is affirmative, thank goodness! There are even several ways to fulfill the task. One of the conceptual keys to the solution had already been outlined by J. W. Gibbs in his famous book about statistical mechanics [17]. Specifically, he was one of the true adepts of the atomistic hypothesis, and had described his standpoint as follows:

… The laws of thermodynamics may be easily obtained from the principles of statistical mechanics, of which they are the incomplete expression, but they make a somewhat blind guide in our search for those laws. This is perhaps the principal cause of the slow progress of rational thermodynamics, as contrasted with the rapid deduction of the consequences of its laws as empirically established.

We may, therefore, confidently believe that nothing will more conduce to the clear apprehension of the relation of thermodynamics to rational mechanics, and to the interpretation of observed phenomena, with reference to their evidence respecting the molecular constitution of bodies, than the study of the fundamental notions and principles of that department of mechanics to which thermodynamics is especially related.

Moreover, we avoid the gravest difficulties when giving up the attempt to frame hypotheses concerning the constitution of material bodies, we pursue statistical inquiries as a branch of rational mechanics. In the present state of science, it seems hardly possible to frame a dynamic theory of molecular action which shall embrace the phenomena of thermodynamics, of radiation, and of the electrical manifestations which accompany the union of atoms, Yet any theory is obviously inadequate, which does not take account of all these phenomena. Even if we confine our attention to the phenomena distinctively thermodynamic, we do not escape difficulties in as simple a matter as the number of degrees of freedom of a diatomic gas. It is well known that while theory would assign to the gas six degrees of freedom per molecule, in our experiments on specific heat, we cannot account for more than five. Certainly, one is building on an insecure foundation, who rests his work on hypotheses concerning the constitution of matter.

Difficulties of this kind have deterred the author from attempting to explain the mysteries of nature, and have forced him to be contented with the more modest aim of deducing some of the more obvious propositions relating to the statistical branch of mechanics. Here, there can be no mistake in regard to the agreement of the hypotheses with the facts of nature, for nothing is assumed in that respect. The only error into which one can fall is the want of agreement between the premises and the conclusions, and this, with care, one may hope, in the main, to avoid".

J. W. Gibbs had clearly and logically perfect shown how the notion of probability could in principle be introduced, when studying thermodynamics, as well as the (everlasting) difficulties in connection with such an approach. Well, it is clear that we are capable of introducing the probability notion into the field of thermodynamics via statistical mechanics–there is surely nothing impossible–this is an absolutely valid way. But this doesn't exclude the possibility to go other possible and logically valid ways as well! The first and foremost difficulty in this respect is to conclusively define, what the true meaning of the probability notion is in fact. Still, this is a rather complicated philosophical question which is until nowadays rather far from being satisfactorily solved! Prof. Dr. Hans-Otto Georgii (LMU, Munich, Germany), a mathematician, describes the situation in his book by

Georgii [18] as follows (Georgii's book is published in German, so that here is my authorized English translation):

…*What is actually 'a chance', etc. etc. etc., 'random'? This is a deep philosophical question that is not yet satisfactorily resolved: Whether "The Lord plays dice" or in fact not (as Albert Einstein had once stated apodictically), whether random events are only apparent and due to our partial ignorance, or whether the accident is a natural inherent phenomenon–we have still no definitive answers to such questions*".

Some similar notes can also be found already in the book by Gibbs [17], namely:

"*...The application of this principle is not limited to cases in which there is a formal and explicit reference to an ensemble of systems. Yet the conception of such an ensemble may serve to give precision to notions of probability. It is in fact customary in the discussion of probabilities to describe anything which is imperfectly known as something taken at random from a great number of things which are completely described*".

Thus, by and large, what kind of conclusion should we, the readership, draw as concerns the notion of probability? To sum up, there are two major standpoints as for the latter, namely, the 'subjective' (or–better to express it–'logical') one and the 'objective' one. Well, the both seem to have the full right to exist and to be employed, when dealing with the actual happenings. The researchers' task would then be to find the formal mathematical interconnections between the results obtained using the both. Still, the modern physics and chemistry are largely based upon the 'objective' standpoint as concerns the probability notion–the latter is conventionally connected with the statistical mechanics based upon the microscopic considerations, in line with the (by now) really widespread and deeply rooted atomistic representation of the structure of matter… Meanwhile, of real interest and importance would also be the attempts to reach the same conclusions by going other ways! To this end, the 'subjective, i.e. logical standpoint' as to the 'physical probabilities' isn't by far conventional nowadays, but shouldn't be proven to be out of question anyway…

One of the relatively recent examples of the above-mentioned kind is the work by Lavenda [19,20]. He had managed to formally mathematically derive the famous Boltzmann-Plank expression for entropy, as a logarithm of probability without any application to the atomistic representation, but solely using the "Gaussian law of errors". This way, in fact, he could have succeeded in extending the Gibbs' approach [17].

The work of George Augustus Linhart

Meanwhile, there had also been a successful attempt to formally derive the Boltzmann-Plank expression using the purely logical approach to the probability notion–and also without any application to the atomistic representation–by Dr. George Augustus Linhart (1885-1951)–but this remarkable work could find its way to the attention of the scientific community only most recently [21-23]. In connection with G. A. Linhart's work, there is also one point of importance for our present EEC discussion. Specifically, Linhart had suggested a possible answer to the question: "What is entropy?" According to Linhart's ideas, entropy is nothing more than just 'all the possible hindrances to some real physical-chemical progress in question'. Anyway, in every real process, whatever it might be, there are some driving forces which underlie and cause the 'progress', and there are inevitable and ubiquitous 'hindrances' as well, whereas the actual interplay between the latter both determines the actual outcome of the process under study.

Now, the interesting and important issue would be: How could we introduce the probability notion in this case? Well, in view of the above-mentioned 'progress-hindrance' dichotomy–or we might even say, *'progress-hindrance' dialectics–we definitely know that 'there ought to be at least some result of the process under study'*-and this should anyway be the only certain outcome. The Czech humorist and satirist Jaroslav Hashek had put this idea in his famous book '*The Good Soldier Shvejk*' as follows:

At' si bylo, jak si bylo, prece jaksi bylo, Jeste nikdy nebylo, aby jaksi nebylo.

"It was just how it was, yet somehow it was. But it's never been so that it was in no way"

What we cannot faithfully foretell in many cases sounds this way: which exactly outcome might we get out of the process under study? … Still, there certainly might be two possibilities (at the minimum!): we do get right what we expect–or just the contrary. To this end, speaking the probabilistic language, we may cast all this in such an assertion: The probability that we observe either the outcome A or the outcome B is equal to 1, the probability that we observe neither A nor B is equal to 0, whereas the probability that we observe exactly A is equal to $0 \le p \le 1$ –and the probability that we observe exactly B is equal to 1–p. Hence, the task for the researchers would now be to somehow find the formal mathematical expression for the p and use it in solving further tasks … This is, in effect, just what had been accomplished by G. A. Linhart. Moreover, he could really extend the meaning of the entropy notion starting from its conventional thermodynamic definition (what we know as the Clausius' formula)–and thus, formally embody the well-recognized 'entropy's anthropomorphism' …

The physical-chemical sense of the valid EEC

With all this in mind, we might find an interesting parallel to the assertion of the work [2]: "*Total entropy (the entropy of the system under study plus the entropy of the system's environment–my insertion will always increase as an accompaniment to a real change, but remain fixed for a system that doesn't change*". The authors [2] obviously derive the latter statement from the general formulation of the Second Law of Thermodynamics, and then refer to the work by M. Planck. Interestingly, the paper [4] follows some similar way of reasoning to reveal a close relationship between the analyses of the Gibbs' free energy and the entropy analyses …

Remarkably, the above-mentioned statement and approaches are in fact inherently related to the reasoning by Starikov [21-23], and could in principle serve as an extension of Planck's reasoning, which had put a remarkable assertion into the introduction to his well known book on thermodynamics [24].

The English translation of that Planck's saying sounds as follows:

"…*When mentioning the recent research results in the area of thermal radiation, I would here point only to the names of W. Wien, F. Paschen, O. Lummer and E. Pringsheim, H. Rubens and F. Kurlbaum. Anyway, these results have allowed us to more and more clearly recognize that the first law of thermodynamics is only one side of the universal principle of conservation of energy, just like the second law, the principle of the entropy increase, has no independent meaning, but its full contents ought to be understood, as soon as its roots are recognized in the well-known theorems of probability theory, according to the representation introduced by Clausius and Maxwell, and then notably developed by L. Boltzmann. According to the latter viewpoint, the entropy of any natural state is, in general, equal to the logarithm of the "probability" of the pertinent state, times some universal constant with the dimension of energy divided by temperature. A more detailed* *discussion of this relationship would be in order, which enables us to gain a deeper than ever insight into the molecular processes, as well as into the laws of radiation. Meanwhile, this would exceed the clearly defined framework of the present publication just from the outset–and, therefore, has not been included here, especially since I plan to treat these topics in a separate book*".

Aside from the well-known idea about the essential interrelationship between the entropy and probability notions, this fragment represents a clear hint at the intrinsic interconnection between the first and the second thermodynamics laws–but, to our regret, M. Planck hadn't specified, how exactly this interrelationship ought to look like …

…Now, let us come back to the paper [2]. The authors start out from the well-known book by Lewis et al. [25], and remind that the notion of the free energy, 'the Gibbs and Helmholtz functions' is widely used in physical-chemical research as a convenient representation of equilibrium constants for diverse chemical reactions. Still, their criticism as concerns the usage of free energy is fully justified–they note that "…*it is not the logics of the Gibbs function that is being questioned, but rather its suitability to the effort of helping students understand the nature of chemical reactions*". One of the significant points, according to Strong and Halliwell [2], consists in that "*the Gibbs function tended to be regarded as a 'free energy' is not truly an 'energy'* ..."–and, following this train of thoughts, they manage to establish an intrinsic interrelationship between the energy and entropy. Then, Strong and Halliwell [2] start their deliberations on the possible driving forces for the actual physical-chemical processes, based upon the first law of thermodynamics, and draw the conclusion that "…*redistribution of energy accompanying a change in state is probably the simplest example of the way energy redistribution accompanies every change. It is energy redistribution that is significant, not any change in the magnitude of the energy*".

In fact, we could interpret the above-formulated standpoint as follows: the general conservation of energy principle ought to dictate that, to create a driving force for some realistic process (enabling the change of the system's initial state–or, otherwise, creating the source of the 'progress' in the process under study, if we put this using the words of G. A. Linhart), it is enough to purposefully trigger a conversion of one type energy into another one. And then the paper states: "…*'free energy' seems to serve as a source of confusion because it gives the illusion of focusing all the attention on energy to the exclusion of entropy*" [2]. Meanwhile, Strong and Halliwell [2] note: "…the distribution of energy within a system is usually represented by an entropy function". Consequently, the above-mentioned 'redistribution of energy' cannot run without entropy as well–and this is exactly where the interrelationship between the first and the second law of thermodynamics, as mentioned by M. Planck, should at last come into play … The paper briefly summarizes such a consideration, concerning real chemical processes, as follows: "why does a reaction go and then stop?" [2]. In this connection, Strong and Halliwell [2] refer to the second law of thermodynamics and present their answer to the question: "*A reaction proceeds when there is a process available that leads to an increase in total entropy, and the reaction stops when no way is open to total entropy increase*". The rest of the paper [2] is devoted to formulating the expression for the 'total entropy', which is dubbed, 'the Planck function', after referring to book by Planck [24].

And–to sum up–what we, the readership are remaining with: we are now possessed of nothing more than just a formal, 'mechanical exchange' of the notion: 'free energy' for the notion: 'total entropy'–but we still haven't learned anything about the physical-chemical sense of the thermodynamic notions of energy and entropy, respectively, about the sense of the interconnection between the first and the second laws of thermodynamics–and the paper [4] doesn't add anything to the latter picture. In the same vein, from the paper [3], we learn that entropy is not 'randomness' or 'disorder' of any kind … but we still cannot recognize any sensible physical-chemical meaning of the entropy notion …

… Here, a familiarity with G. A. Linhart's ideas may perhaps help to easily resolve the problem, for; in fact, we are already right in the nearest vicinity of its complete solution. Thus, let us put all the above deliberations together–but now adding just a little bit of healthy logics:

1. The driving force for the process of our interest comes from a redistribution of energy and ensures the progress of the process under consideration;
2. Any progress in the nature ought to meet hindrances (of whatever kind); zero progress would obviously meet zero hindrances;
3. The higher the progress, the higher the hindrances (the hindrances ought to somehow increase together with the increase in the progress);
4. Any progress would never stop without any active hindrance; hence, the process would anyway come to its end, that is, to some sensible result, as soon as the progress and the hindrances equilibrate each other somehow.

By and large, there is a truly dialectic interrelationship between the 'energy redistribution' and the 'total entropy change'. The latter both are inherently similar to the 'Yin' and 'Yang' of the traditional Chinese philosophy, therewith delivering the everlasting "unity and struggle of opposites", and suggesting the true nature of interrelationship between the first and the second laws of thermodynamics. It is really senseless to separate the one from another, like it is still done–conventionally and steadily …

To this end, the physical-chemical sense of the valid EEC phenomena ought to be throughout clear: the latter are capable of embodying the true versatility of mechanisms that underlie the processes in question.

How we can use the physically-chemically valid EEC concept when interpreting experimental data

Thus, first of all we would like to take into account the parallel between the notion of EEC and the Carnot cycle. In fact, it is well known that the true, conventional Carnot cycle consists of four basic steps:

a. reversible isothermal expansion of the gas at the 'hot' temperature, T_H (in other words, isothermal heat addition or absorption);
b. isentropic (in other words, reversible adiabatic) expansion of gas (isentropic work output);
c. reversible isothermal compression of the gas at the 'cold' temperature, T_C-where $T_C<T_H$;
d. isentropic compression of the gas (in other words, reversible adiabatic work input).

In our earlier work [8], we could rigorously show that it is just the position of the so-called 'enthalpy–entropy compensation temperature' with respect to the lab temperature, which is immensely helpful in introducing something like a thermodynamical cycle (hidden, 'imaginary'–or even explicit, depending on the exact experimental conditions), essentially similar to the classical Carnot cycle.

Therefore, the EEC concept turns out to bear not only a purely philosophic and academic significance, but might be a handy, versatile and powerful tool in interpreting systematic physical-chemical

Citation: Starikov EB (2013) Entropy-Enthalpy Compensation and Its Significance in Particular for Nanoscale Events. 2: 624 doi:10.4172/scientificreports.624

experimental data, as well. Here we would only like to present a simple interpretational algorithm:

1. Thorough and systematical experimental data on EEC must first be obtained. But, mind that not every experimentally revealed EEC is a valid one [5-7]. Typically, one must use independent experimental approaches for one and the same specimen (set of specimens) to get enthalpy and entropy. If the latter both are obtained, say as a result of the conventional Arrhenius or van't Hoff analyses, this is not a physically-chemically interpretable EEC.
2. The conventional linear regression of the experimental enthalpy on the experimental entropy data must be found in the standard way, to reliably evaluate the a and T_c parameters in Equation 1. Only then, the "Carnot entropic parameter", a/T_c, can be determined.
3. The results thus obtained can be interpreted using own experimental data and the information known from the literature.

The algorithm is pretty easy in itself, with the third step being definitely the most non-trivial one. But this should not constitute any "inviolable fortification" for the specialists in the respective fields. A more detailed analysis and the corresponding examples could be borrowed from our recent publications [8,26,27], and the references therein).

Thermodynamics at nanoscale

Here we would just like to present a mini-review of the recent works dealing with the thermodynamics at the microscopic level.

First, it should be mentioned that already such notions and standpoints of the conventional thermodynamics as 'equilibrium' and 'reversibility' are being essentially revised. For example, the work by Jarzynski [28] and the references therein, is devoted to detailed microscopic analyses of a general thermodynamic process, which conventionally, brings a system from one equilibrium state to another one, so that the ensemble of microscopic realizations of the process under study would depend only of its equilibrium start and end states, even if all the intermediate stages are out of equilibrium. This result could be used to express the entropy difference between two equilibrium states, in terms of an irreversible process connecting them–and finally, boils down to two specific statistical interpretations of the Clausius-Duhem inequality for entropy (as the conventional statement of the second law of thermodynamics), and might be generalized to situations when the process of interest both begins, and/or ends up in non-equilibrium states, either way.

As to the conventional thermodynamical concept of 'reversibility', it is known to be essential to the subject of the conventional equilibrium thermodynamics, but it is anyway fully abstract and idealistic (it is being practically used only to begin with the rigorous mathematical considerations in the field), for it is a well-known matter of our everyday experience that all processes in the real world surrounding us are in effect irreversible [29]. However, the latter representation is still far away from what is being actually taught in the standard thermodynamics books [30].

Of immense interest for–and direct relevance to–our present topic is anyway the on-going work to apply thermodynamic concepts and notions at the supramolecular level–this is important for consistently interpreting the data of diverse experimental single-molecule measurements [31-35].

Micro-phase transitions

We have discussed the relationship between the micro-phase transitions and the EEC phenomena in our earlier publications [8,26,27]. Here, we would only like to point out the difference between the conventional 'phase transitions' and the 'microphase transitions'. For this purpose, we might consider some examples from the book by Dill and Bromberg [36], and the review [37]. Specifically, if we heat water up to its boiling point, we shall massively drive water into its gaseous state, so that the water's density will tremendously decrease and the unique liquid properties will be lost. But, if we consider the same process at a temperature far away from the boiling point, the density decrease would come to only up to several tenth of percent and the water remains liquid. This difference between the gradual change of some integral parameter (the latter situation) and its sharp change (the former situation) does characterize the conventional phase transitions. While the conventional phase transitions have to do with the global changes in interatomic/intermolecular behaviour, there could also be some rather sharp changes in properties of single molecules (if we take into consideration macromolecules like biopolymers, for example–this ought to be the so-called 'cooperative processes' in such systems)–or just in some specific areas of the system, like surface effects, which at the same time don't involve the rest of the system. We could in principle, consider the latter cases as 'micro-phase transitions', that is, the phase transitions of more or less restricted scale.

Still, as we have learned from the papers [31-35], it is throughout possible to apply the conventional thermodynamics to diverse systems of macromolecular level–and this brings sound results. This is why; we may also successfully use the well-known thermodynamical notions and concepts in studying the micro-phase transition phenomena, and/or similar events.

A propos, the book by Dill and Bromberg [36] contains detailed and useful discussions about the sense of the chance, probability, entropy, etc. notions, as well–but the 'gravitation' from the conventional standpoints is obviously enormous to the extent that all the everlasting 'misconceptions' (as A. Ben-Naim nicely puts this) are still alive, and–to wit–to 100% present … Well-well, so how many generations ought to wait for the final triumph of the true physical-chemical notions and concepts? God knows, God knows … Right as B. H. Lavenda had very appropriately expressed it [19]: "… *This just points to the vacuum in which physicists work and the high degree of patronization that there is in science today* …." After attentively reading the articles by chemists [2-4] and comparing them in detail with the stories by physicists [38-40], the above conclusion by B. H. Lavenda looks like being applicable not only to physics, but to chemistry as well … The valuable warning by Gibbs [17]: "*The only error into which one can fall, is the want of agreement between the premises and the conclusions, and this, with care, one may hope in the main, to avoid*". seems to have slowly-slowly stumbled into a complete oblivion …

And, bearing all this in mind, how could the EEC concept described above is practically used to interpret the particular experimental data at microscopic level? We have most recently presented a detailed overview of this very interesting, important topic [41], and would like to refer the interested readership to this overview. We are presently continuing our work to establish the valid interconnections between the EEC concept, and the molecular/atomic structure of the matter, and will report our further results elsewhere.

Conclusion

We hope to have demonstrated that a description of enthalpy-entropy compensation in a general format (general EEC) is never in conflict with the conventional thermodynamics, and can in principle, be derived in an exact way using statistical thermodynamics. Taken together with the work of other authors, our analysis constitutes a proof of a general theorem that connects a valid, non-trivial EEC with thermodynamic (Carnot), or even kinetic cycles of the similar kind. The latter approach can definitely be of great mechanistic-diagnostic value, for example, useful in nanoscience, when considering working efficiencies of molecular motors, ratchets, heat pumps, and/or refrigerators at micro- and mesoscopic level, so that a clever use of thoughtfully composed combinations of well-established experimental methods might definitely be of immense help. With this in mind, other potential applications of the EEC phenomena might include the characterization of microscopic hidden structures and processes, like (micro-)phase transitions, which are definitely useful for the mechanistic interpretation of thermodynamic, and/or kinetic activation parameters in complex nanolevel systems of any kind.

References

1. http://en.wikipedia.org/wiki/Enthalpy-entropy_compensation
2. Strong LE, Halliwell HF (1970) An alternative to free energy for undergraduate instruction. J Chem Educ 47: 347-352.
3. Lowe JP (1988) Entropy: Conceptual disorder. J Chem Educ 65: 403-406.
4. Craig NC (1988) Entropy analyses of four familiar processes. J Chem Educ 65: 760-764.
5. Cornish-Bowden A (2002) Enthalpy–entropy compensation: a phantom phenomenon. J Biosci 27: 121-126.
6. Liu L, Guo QX (2001) Isokinetic relationship, isoequilibrium relationship, and enthalpy-entropy compensation. Chem Rev 101: 673-695.
7. Cooper A, Johnson CM, Lakey JH, Nöllmann M (2001) Heat does not come in different colours: entropy-enthalpy compensation, free energy windows, quantum confinement, pressure perturbation calorimetry, solvation and the multiple causes of heat capacity effects in biomolecular interactions. Biophys Chem 93: 215-230.
8. Starikov EB, Nordén B (2007) Enthalpy-entropy compensation: a phantom or something useful? J Phys Chem B 111: 14431-14435.
9. Müller I, Weiss W (2005) Entropy and Energy: A Universal Competition. Springer, Berlin & Heidelberg, Germany.
10. Fermi E (1956) Thermodynamics. Dover Publications, New York, USA.
11. Ben-Naim A (2008) Entropy Demystified. World Scientific Publishing, Singapore.
12. Ben-Naim A (2008) A farewell to entropy: Statistical Thermodynamics based on information. World Scientific Publishing, Singapore.
13. Ben-Naim A (2010) Discover entropy and the second law of thermodynamics: A playful way of discovering a law of nature. World Scientific Publishing, Singapore.
14. Ben-Naim A (2012) Entropy and the Second Law: Interpretation and Misss-Interpretationsss. World Scientific Publishing, Singapore.
15. Shannon CA, Weaver W (1971) The mathematical theory of communication. The University of Illinois Press, Urbana, USA.
16. Reza FM (1961) An introduction to information theory. McGraw-Hill, New York, USA.
17. Gibbs JW (1902) Elementary principles in statistical mechanics. Scribner's Sons, New York, USA.
18. Georgii HO (2009) Stochastics: Introduction to probability and statistics. Walter de Gruyter, Berlin, Germany, New York, USA.
19. Lavenda BH (1991) Statistical physics: A probabilistic approach. John Wiley & Sons, New York, USA.
20. Lavenda BH (2010) A new perspective on thermodynamics. Springer, New York, USA.
21. Starikov EB (2010) Many faces of entropy or Bayesian statistical mechanics. Chem Phys Chem 11: 3387-3394.
22. Starikov EB (2012) George Augustus Linhart – As a "Widely Unknown" Thermodynamicist. World J Cond Matt Phys 2: 101-116.
23. Starikov EB (2013)'Entropy is anthropomorphic': does this lead to interpretational devalorisation of entropy-enthalpy compensation? Monatsh Chem 144: 97-102.
24. Planck M (1922) Lectures on thermodynamics. Walter de Gruyter, Berlin, Leipzig, Germany.
25. Lewis GN, Randall M, Pitzer KS, Brewer L (1961) Thermodynamics. McGraw-Hill Book Company, New York, USA.
26. Starikov EB, Nordén B (2012) Entropy-enthalpy compensation may be a useful interpretation tool for complex systems like protein-DNA complexes: An appeal to experimentalists. Appl Phys Lett 100: 193701.
27. Starikov EB, Nordén B (2012) Entropy-enthalpy compensation as a fundamental concept and analysis tool for systematical experimental data. Chem Phys Lett 538: 118-120.
28. Jarzynski C (1999) Microscopic analysis of Clausius Duhem processes. J Stat Phys 96: 415-427.
29. Van Ness HC (1983) Understanding Thermodynamics. Dover Publications, New York, USA.
30. Smith EB (2004) Basic chemical thermodynamics. (5th Edn), World Scientific Publishing, Singapore.
31. Dhar A, Chaudhuri D (2002) Triple minima in the free energy of semiflexible polymers. Phys Rev Lett 89: 065502.
32. Sinha S, Samuel J (2005) Inequivalence of statistical ensembles in single molecule measurements. Phys Rev E 71: 021104.
33. Sinha S (2008) Free energy of twisted semiflexible polymers. Phys Rev E 77: 061903.
34. Süzen M, Sega M, Holm C (2009) Ensemble inequivalence in single molecule experiments. Phys Rev E 79: 051118.
35. Kozlovskii MP, Romanik RV (2011) Gibbs free energy and Helmholtz free energy for a three-dimensional Ising-like model. Cond Matt Phys 14: 43002.
36. Dill KA, Bromberg S (2010) Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry Physics, and Nanoscience. (2nd Edn), Taylor & Francis, New York, USA.
37. Tartaglino U, Zykova-Timan T, Ercolessi F, Tosatti E (2005) Melting and nonmelting of solid surfaces and nanosystems. Phys Rep 411: 291-321.
38. Andrew K (1984) Entropy. Am J Phys 52: 492-496.
39. Baierlein R (1994) Entropy and the second law: A pedagogical alternative. Am J Phys 62: 15-26.
40. Moore TA, Schroeder DV (1997) A different approach to introducing statistical mechanics. Am J Phys 65: 26-36.
41. Starikov EB, Nordén B (2012) Entropy-Enthalpy compensation: Is there an underlying microscopic mechanism? Current Microscopy Contributions to Advances in Science and Technology, (Méndez-Vilas A ed.), Formatex Research Center, Spain 2: 1492-1503.