3RD INTERNATIONAL EXERGY, LIFE CYCLE ASSESSMENT & SUSTAINABILITY WORKSHOP & SYMPOSIUM

ELCAS

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07- 09 JULY 2013
NISYROS ISLAND, GREECE

Under the Frame of:

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EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

Smart Energy Regions

Edited by:

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ELCAS 3, 07- 09 JULY 2013, NISYROS ISLAND, GREECE

EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

COST TU1104-SMART ENERGY REGIONS

PROCEEDINGS OF ELCAS 2013

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SALUTATION BY THE CHAIRMAN OF ELCAS

The Third International Exergy, Life Cycle Assessment and Sustainability Workshop & Symposium (ELCAS) is the concrete proof that the effort to bring together scientists dealing with the issues of Exergy Analysis, Life Cycle Assessment and issues of sustainability will go on. ECLAS is a multidisciplinary / interdisciplinary international conference and provides a forum for researchers, scientists, engineers and practitioners from all over the world to disseminate information, present new ideas and developments, and discuss the future direction and priorities in the fields of exergy, Life Cycle Assessment and Sustainability.

The third ELCAS is a COST TU1104 conference with the objective to give an opportunity to all its members and many other scientists to come together for the exchange of ideas.

Our expectation from this Symposium is very high, since the outcome of the presentations and discussions will be fruitful for academia and industry. Moreover, it is expected to serve as nourishment to the cooperation between academia and industry in terms of developing research programs in various areas of exergy, energy and sustainability. It will also give a lot of food for thought for the young researchers who attend this event.

ELCAS has received considerable international attention. The number of abstracts received and the vast number of countries represented at the symposium is indicative of the international attention it has received. In addition, ELCAS features keynote lectures by well-respected scholars. It now provides an exciting technical program encompassing a wide range of topics ranging from exergy to environmental impact.

It is a common knowledge that the efforts required in organizing and holding such a Symposium are extensive. This workshop and Symposium ELCAS could not have been organized without economic support from the Cost Action TU1104 Smart Energy Regions, and I am grateful, expressing the feelings of all the participants. I want to thank all the members of the COST Action TU1104 for their collaboration. It is a great pleasure to collaborate with the science officer of the Action Dr. Thierry Goger. Phil Jones, the chairman of the action is an inspiring force behind all the efforts for the success of the TU1104. Joanne Paterson, the responsible person for the day to day affairs of the action has been extremely helpful.

I am grateful to my colleagues Aris Dompros, Dimitri Rovas and Eva Nanaki who have worked tirelessly for the success of the symposium. I would like to thank the Local Organizing Committee Members for their excellent job in making local preparations and arrangements. I would like to take this opportunity to express my appreciation to the Honorary Chair, Technical Chairs and International Scientific and Advisory Committee Members for their promotion and contribution. I would like to register my sincere appreciation to the municipality of Nisyros for the valuable support given to the organizing committee. Last, but not least, I acknowledge my gratitude to the ELCAS keynote speakers, authors, session chairpersons and attendees whose contributions and efforts have made this success possible.

Prof. Christopher Koroneos

Vice Chairman of COST Action TU1104

Chairman of ELCAS

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KEYNOTE SPEECHES

	ORAL PRESENTATIONS – KEYNOTE SPEECHES	

LIFE CYCLE SUSTAINABILITY ASSESSMENT

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1. Sustainable development

Sustainability has become a much used and ill defined term, meaning everything from "environmental friendly", "green", "low carbon" to "constant economic growth rates". In order to quantify sustainability the term has to be explained and its use has to be restricted, here to **product systems** as in Life Cycle Assessment (LCA) [1-3]. Products in this sense (ISO 14040:2006; 14044:2006) are goods and services, the system extends from cradle-to-grave. Products fulfilling the same or a very similar function can by compared by means of a "functional unit". The comparison is restricted in LCA to the environmental aspects. If we try to define sustainability in such a way as to make comparisons possible, we will be guided by methods and definitions used in LCA, but extend them to the broader field of sustainability. But what means "sustainable"? We will see that the word is very old, but its use in modern times goes back to the "Brundtland report" on "sustainable development" [4]. The famous definition reads as follows:

"Sustainable development is development that meets the needs of present without compromising the ability of future generations to meet their own needs"

For the purpose outlined above we have to operationalize the terms sustainable and sustainability in the spirit of the definition and other developments which took place at the same time, i.e. the mid 1980s. Life cycle assessment did already exist at that time – before the name coined by SETAC - in the form of relatively simple cradle-to-grave methods for comparative environmental analyses. I called these precursor methods "Proto-LCAs" [5]. Life Cycle Costing (LCC), the economic equivalent to LCA, is older [1,6]. One of the influential developments was a method called "Produktlinienanalyse", by a working group of Oekoinstitut Freiburg [7]. This was a Proto-LCA enriched by two further LCA-type analyses, LCC and an early social LCA. This was the birth of the "three pillar" model (see below). The modern version of the Oekoinstitut-method is called Product Sustainability Analysis (PROSA) [8].

2. Origin of the term "Sustainability"

A short excursus into history shows that the idea of sustainability comes from forestry management and is connected with the name of Hans Carl von Carlowitz. He was the director of the Saxonian silver mines in the early 18th century and in this function he

needed a lot of timber. In addition he was a forest scientist and published a famous book exactly 300 years ago [9]. In this book he described in detail how forests should be managed in order to last for centuries and called this method "nachhaltig". This was the basis for improving the forestry first in Germany (the forests were in a very bad shape during Carlowitz´ lifetime) and later on in Switzerland and France. In this way, "nachhaltig" became "soutenue" and, later, "sustainable" [10].

Today, the French speakers mostly use the term "durable". Grober [10] followed up the term from Carlowitz to Brundtland. Reading carefully the book by Carlowitz shows that not only economic topics are addressed, but also environmental issues – as we would say today – and even some social aspects.

The further career of the term sustainability is well known: the UNEP conferences in Rio de Janeiro (1992) and Johannesburg (2002) declared sustainability as the most important concept for the 21st Century and even a connection with Life cycle thinking was recommended. It is certainly not by chance that 2002, just before the Johannesburg conference, the UNEP/SETAC Life Cycle Initiative was founded [11]. From now on, sustainability and LC-methods have been discussed together.

3.   Personal experiences with product systems and the three pillar concept

How did I become aware of the problems connected with sustainability assessment of product systems? The method by Oekoinstitut has already been mentioned. The next step was the EuroMat project [12]. Under the leadership of Prof. Fleischer (TU Berlin), several German research institutes, companies and LCA practitioners developed an LC instrument with more than three components, including also technical and workplace aspects . Co-ordinators of EuroMat were Wulf-Peter Schmidt, Gerald Rebitzer and Kerstin Lichtenvort 1994-2001.

A major breakthrough was the 1st Life Cycle Management (LCM) Conference, Copenhagen 2001, organised by Allan Astrup Jensen. It turned out that partly inconsistent system boundaries were used for the „triple bottom line" concept. This drew my attention to the importance of consistent system boundaries of LCA, LCC and SLCA (see below). What seemed to be a revolution at that time: the broad application of LCM in industry, is now daily praxis in many companies.

The first presentation of my ideas on sustainability assessment was in Athens 2003 [13], published as editorial for the LCM section of Int. J. Life Cycle Assess. [14] with input by Gerald Rebitzer (at that time EPFL, Lausanne). Our main request on a future LC-method for sustainability assessment: consistent, ideally identical system boundaries of the environmental, economic and social LC assessments (see below)!

The next important step was a presentation at the 3rd LCM conference in Zürich 2007, published as peer-reviewed paper in Int. J. Life Cycle Assess. [15]. "Naming of the child": **Life Cycle Sustainability Assessment**, with the acronym LCSA, was proposed by Isa

Renner and Matthias Finkbeiner ("SustAss", still used in the Zürich paper, was removed). LCSA has been used in all further publications, including the landmark UNEP/SETAC-guidance on LCSA in 2011 [16].

Parallel to the previous activities, a SETAC working group on Environmental Life Cycle Costing explored the possibilities of including LCC into sustainability assessment, resulting in a first book on this topic by Hunkeler et al. [17]. This and first results of the LCC guideline writing group were presented at the 5th SETAC World Conference in Sydney 2007 [18,19]. Finally, the SETAC Environmental LCC "code of practice" (Swarr et al.), was published by SETAC Press 2011 [20].

The **three pillar concept** became known under different popular/trivial names, such as "triple bottom line" or "people, planet, profit (PPP)". A convincing procedure is still missing, but I think most people now agree that only life cycle-based methods are suitable as the "pillars".

The shortest way to summarise LCSA within the three pillar concept is a definition based on (environmental) LCA, (environmental) LCC and social LCA, where the "+" signs are, of course, only symbolic (no sustainability points!):

LCSA = LCA + LCC + SLCA (1)

LCA: Environmental **L**ife **C**ycle **A**ssessment

LCC: Environmental (LCA-type) **L**ife **C**ycle **C**osting

SLCA: **S**ocial **L**ife **C**ycle **A**ssessment

There are a few prerequisites, however:

- Consistent system boundaries for the three life cycle methods, using
- the physical (not the marketing-) life cycle („from cradle to grave") and
- compatible inventories (LCI) for the 3 methods (SLCA will in most cases require a better regional resolution compared to the environmental LCA)

We are now in a position to have guidelines for all three components, but the degree of harmonization is different: It is highest for LCA with two very successful international standards ISO 14040:2006 and 14044:2006. Matthias Finkbeiner recently called them the "Constitution of LCA" [21]. The general standard 14040 is also the "mother" of several other LC standards.

For the environmental LCC there is now a "code of practice" available [20]. This name was chosen with purpose, since it is the same as the one used for the SETAC LCA code of practice of 1993 [22]. This document, also called "Sesimbra protocol", was used as "blueprint" for the first series of LCA standards (ISO 14040-14043, Geneva 1997-2000).

The Social LCA has been harmonized as a UNEP/SETAC guideline (2008) [23,24] which is quite broad, too broad perhaps for a future product systems standard.

The LCSA finally got a kind of framework, recently published at the UNEP/SETAC website [16]. It is based on the three pillar concept of product sustainability, as developed by Klöpffer, Renner, Finkbeiner, Rebitzer, Lichtenvort, Hunkeler and others [6-8, 13-15, 17, 20, 25, 26].

4. Standardization of LCSA

There are at least 4 possibilities to standardise LCSA in accordance with ISO. The question is which one should be pursued?

Option 1 corresponds to formula (1). This is my preferred option for reasons of transparency and flexibility. It contains three Life cycle assessments with compatible, ideally identical system boundaries and the same functional unit. Weighting and aggregation should be discouraged.

Option 2

LCSA = "LCA new" (2)

This option "LCA new" would require a complete revision of ISO 14040 and 14044, adding LCC to the Life cycle inventory and SLCA to LCI and Life Cycle Impact Assessment. Since several other LC standards refer to ISO 14040 as the "mother standard", this reference would become obsolete. A weakening of the whole 14040 "family" would be the consequence. In my view, following this option would be counter-productive.

Option 3

LCSA = Eco-efficiency + SLCA (3)

Eco-efficiency = LCA + „Value"

Combining the environmental and the economic pillar may result in "Eco-efficieny" for which recently an ISO standard has become available, ISO 14045:2012. In this standard LCC is replaced by "value", a broader term which can optionally be quantified in monetary units, including LCC results.

It seems that this option is favoured by some industrial users and may be seen as part of LCM. The BASF eco-efficiency method and SEEbalance$^{®}$ [27-30], although developed before ISO 14045, seems to fit into option 3.

Option 4

LCSA = LCA + Socio-economic Analysis (4)

This second „dualistic" solution has been proposed by IFEU (Heidelberg) and is also proposed in a non-official text by the Austrian ministry of the environment.

Due to the combination of the economic and the social component, the economic component is not stated explicitly what seems to be the purpose of this exercise.

It should be noted, however, that the proposed structure was not necessarily aimed at product systems ("meso" in the CALCAS [31] terminology: micro = products; meso = companies; macro = national/global economy).

This option may be appreciated by green movements.

Final look at ISO 14040

- LCA addresses the **environmental aspects and potential impacts**...throughout a product´s life cycle from raw material acquisition through production, use, end-of-life treatment, recycling and final disposal (i.e. cradle-to-grave).
- LCA typically does **not** address the economic or social aspects of a product, but the life cycle approach and methodologies described in this International Standard **may be applied to these other aspects.**

Although not addressed directly, this statement could be seen as an invitation to extend the original environmental LCA toward a more holistic assessment along the basic structure of the very successful standard ISO14040. Indirectly it favours Option1.

We are now in a learning process which not only concerns LCSA, but also the not yet fully developed components LCC and SLCA. With regard to The International Journal of Life Cycle Assessment I can promise that we will accompany this process, but it is clear that this journal is devoted to LCA and closely related methods. There are other environmental assessment journals not so intimately connected to LCA, so that alternative approaches may find a home there.

References

[1]. Curran, Mary Ann (ed.): Life Cycle Assessment Handbook. A Guide for Environmentally Sustainable Products. Wiley-Scivener 2012
[2]. Klöpffer, W.; Grahl, B.: Life Cycle Assessment (LCA) - A guide to best practice. Wiley-VCH, Weinheim. To appear 2013/1
[3]. Klöpffer, W. and Curran, M.A. (eds.) (2013): Encyclopedia of Life Cycle Assessment, Vol. 1. Springer
[4]. WCED - World Commission on Environment and Development: Our Common Future. Oxford 1987
[5]. Klöpffer, W. (2006): The Role of SETAC in the Development of LCA. Int. J. Life Cycle Assess. 11 (Supplement 1), 116-122
[6]. Hunkeler, D.; Lichtenvort, K.; Rebitzer, G. (Eds.): Environmental Life Cycle Costing. SETAC, CRC Press, Boca Raton, Florida 2008
[7]. Projektgruppe ökologische Wirtschaft (Ed.): Produktlinienanalyse: Bedürfnisse, Produkte und ihre Folgen. Kölner Volksblattverlag, Köln 1987

[8]. Grießhammer, R.; Buchert, M.; Gensch, C.-O.; Hochfeld, C.; Manhart, A.; Reisch, L.; Rüdenauer, I.: PROSA – Product Sustainability Assessment. Öko-Institut e.V., Freiburg (ca. 2010)

[9]. Carlowitz, H.C.: Sylvicultura Oeconomica - Naturmäßige Anweisung zur Wilden Baum-Zucht. Leipzig 1713. Reprint [ISBN 3-86012-115-4]: Freiberg, Saxonia 2000

[10]. Grober Ulrich: Die Entdeckung der Nachhaltigkeit. Kulturgeschichte eines Begriffs. Verlag Antje Kunstmann, München 2010

[11]. Töpfer, K.: The Launch of the UNEP-SETAC Life Cycle Initiative (Prague, April 28 2002). Int. J. Life Cycle Assess. Editorial. 7 (3), 191 (2002)

[12]. Fleischer, Günter (Hrsg.); Becker, J.; Braunmiller, U.; Klocke, F.; Klöpffer, W.; Michaeli, W. (Mithrsg.): Eco-Design. Effiziente Entwicklung nachhaltiger Produkte mit euroMat. Springer, Berlin 1999

[13]. Klöpffer, W. (2003): Life-Cycle Based Methods for Sustainable Product Development. Presented at the HELECO `03, 4th International Exhibition and Conference on Environmental Technology. Athens, 30 January - 2 February 2003. Proceedings-Volume B 355-360

[14]. Klöpffer, W. (2003): Life-Cycle Based Methods for Sustainable Product Development. Editorial for the LCM Section in Int. J. Life Cycle Assess. 8 (3) 157-159

[15]. Klöpffer, W. (2008): Life Cycle Sustainability Assessment of Products. Int. J. Life Cycle Assess. 13 (2) 89-94

[16]. UNEP/SETAC: Valdivia, S.; Ugaya, C.M.L.; Sonnemann, G.; Hildenbrand, J. (eds.): Towards a Life Cycle Sustainability Assessment - Making informed choices on products. ISBN: 978-92-807-3175-0 Paris 2011 (download from http://lcinitiative.unep.fr)

[17]. Hunkeler, D.; Lichtenvort, K.; Rebitzer, G. (Eds.): Environmental Life Cycle Costing. CRC Press, Boca Raton (Fl.) Hunkeler, D.; Lichtenvort, K.; Rebitzer, G. (Eds.): Environmental Life Cycle Costing. CRC Press, 2007

[18]. Hunkeler, D.; Klöpffer, W.; Pesonen, H.; Ciroth, A.; Swarr, T.; Pagan, B.; Itsubo, N.: Life Cycle Costing. SETAC World Congress, Sydney, August 6th, 2008

[19]. Klöpffer, W.: The Role of Life Cycle Costing (LCC) in Life Cycle Sustainability Assessment (LCSA). SETAC World Congress, Sydney, August 6th, 2008

[20]. Swarr, Thomas E.; Hunkeler, David; Klöpffer, Walter; Pesonen, Hanna-Leena; Ciroth, Andreas; Brent, Alan C.; Pagan, Robert: Environmental Life Cycle Costing: A Code of Practice. Published by the Society of Environmental Toxicology and Chemistry. SETAC Press, Pensacola (FL) 2011

[21]. Finkbeiner, M.: From the 40s to the 70s – the future of LCA in the ISO14000 family. Int. J. Life Cycle Assess. 18 (1) 1-4

[22]. Society of Environmental Toxicology and Chemistry (SETAC): Guidelines for Life Cycle Assessment: A "Code of Practice". Edition 1. From the SETAC Workshop held at Sesimbra, Portugal, 31 March - 3 April 1993. Brussels, Belgium, and Pensacola, Florida, USA, August 1993

[23]. UNEP/SETAC (2009): Benoît, C.; Mazijn, B. (eds.): Guidelines for Social Life Cycle Assessment of Products. Paris. 104 pp. Downloaded from http://lcinitiative.unep.fr

[24]. Benoît et al. (2010): Benoît, C.; Norris, G.A.; Valdivia, S.; Ciroth, A.; Moberg, A.; Bos, U.; Prakash, S.; Ugaya, C.; Beck, T.: The Guidelines for Social Life Cycle Assessment of products: Just in time! Int J. Life Cycle Assess, 15 (2) 156-163

[25]. Klöpffer, W.; Renner, I. (2008): Life-Cycle Based Sustainability Assessment of Products. Chapter 5 in: Schaltegger, S.; Bennett, M.; Burritt, R.L.; Jasch, C. (Eds.): Environmental Management Accounting for Cleaner Production. ISBN 978-1- 4020-8912-1. Springer, pp. 91-102

[26]. Finkbeiner, M.; Schau, E.M.; Lehmann, A.; Traverso, M. (2010): Towards Life Cycle Sustainability Assessment. Sustainability 2, 3309-3322; open access doi:10.3390/su2103309

[27]. Saling, P.; Gensch, C.-O.; Kreisel, G.; Kralisch, D.; Diehlmann, A.; Preuße, D.; Meurer, M.; Kölsch, D.; Schmidt, I.: Entwicklung der Nachhaltigkeitsbewertung SEEbalance® - im BMBF-Projekt „Nachhaltige Aromatenchemie". Karlsruher Schriften zur Geographie und Geoökologie. Karlsruhe 2007

[28]. Saling, P.; Kicherer, A.; Dittrich-Krämer, B.; Wittlinger, R.; Zombik, W.; Schmidt, I.; Schrott, W.; Schmidt, S. (2002): Eco-efficiency Analysis by BASF: The method. Int J Life Cycle Assess. 7, 203-218

[29]. Landsiedel, R.; Saling, P. (2002): Assessment of Toxicological Risks for Life Cycle Assessment and Eco-efficiency Analysis. Int. J. LCA 7, 261-268

[30]. Kicherer, A.; Schaltegger, S.; Tschochohei, H.; Ferreira Pozo, B.: Eco-Efficiency. Combining Life Cycle Assessment and Life Cycle Costs via Normalization. Int. J. LCA 12 (7) 537-543

[31]. CALCAS (2009): Zamagni, A.; Buttol, P.; Buonamici, R.; Masoni, P.; Guinée, J.B.; Huppes, G.; Heijungs, R.; E. van der Voet, Ekvall, T.; Rydberg, T.: Co-ordination Action for innovation in Life-Cycle Analysis for Sustainability. D20 Blue Paper on Life Cycle Sustainability Analysis. Revision 1 after the open consultation. August 2009. http://www.estis.net

BREAKING SYMMETRIES
AND EMERGING URBAN STRUCTURES

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Abstract

Like all living organisms, cities are open systems constantly exchanging energy and matter with their environment in order to maintain their existence and create new structures. Flows run through them ceaselessly: people and goods, all forms of energy, water, wind, sun, and natural forces. Open systems cannot be described using classical thermodynamics of equilibrium, as developed in the 19th century by Boltzmann. To understand them, we have to turn to the more recent work of Ilya Prigogine on the theory of dissipative structures, far-from-equilibrium thermodynamics, and self-organizing systems.

The theory of dissipative structures focuses on self-organizing phenomena, on the seemingly spontaneous emergence of an order, that is to say of a spatial and temporal morphology within a system made up of a great number of entities. In all cases, dissipative structures involve a "symmetry break". A homogenous, undifferentiated state (spatially and temporally) gives way to a heterogeneous, differentiated state that is less symmetrical than the prior one.

The urban structures resulting from the maximization of exergy predicted by Prigogine are fractals. They obey scaling laws, that is to say their elements and connections are distributed according to Pareto distributions.

Keywords: *exergy, dissipative systems, urban structures, fractals, Pareto distribution*

1. Introduction: Creating forms by breaking symmetry

Historical cities, over the course of their long history, were slowly transformed by incremental phenomena of destruction and reconstruction of the urban fabric. Structures that were not resilient enough were eliminated. And so historical cities have come down to us with extraordinary capacities of efficiency and resilience. In a process of ongoing, spontaneous self-organization to adapt their forms to fluctuations in their environment, historical cities acquired the capacity to absorb fluctuations by reinforcing their structure and order, and becoming more complex.

1.1. Open systems far from equilibrium

Thermodynamics, a complexity science par excellence, enables us to describe vast systems, sites of numerous microscopic events, flows of energy and matter, by synthesizing them on a global scale by macroscopic parameters. This is exactly what cities are and how they can be described: indescribable in their tiny details, but globally structured by the interactions between their forms and the flows that run through them.

Cities are not closed systems anyway and thus they do not obey the second principle of thermodynamics,[a] and this from the very start, approximately five thousand years ago, when the surpluses produced by improved farming techniques put cities into a creative disequilibrium with their environment.

1.2. Symmetry breaks and the emergence of complexity

As Ilya Prigogine and Isabelle Stengers point out, "Equilibrium structures can be seen as the results of statistical compensation for the activity of microscopic elements (molecules, atoms). By definition they are inert at the global level. For this reason they are also 'immortal'. Once they have been formed, they may be isolated and maintained indefinitely without further interaction with their environment. When we examine a biological cell or a city, however, the situation is quite different: not only are these systems open, but also they exist only because they are open. They feed on the flux of matter and energy coming to them from the outside world. We can isolate a crystal, but cities and cells die when cut off from their environment. They form an integral part of the world from which they draw sustenance, and they cannot be separated from the fluxes that they incessantly transform."[b]

This is a crucial distinction: while classic thermodynamics predicts the dissolution of any ordered structure and the ultimate reduction of any complexity, Prigogine's theory develops the creative potential of non-linear, far-from-equilibrium thermodynamics. "Prigogine shows that the second principle does indeed exclude the emergence of an order when the systems evolve close to thermodynamic equilibrium, but this is no longer the case far from equilibrium. More precisely, the passage from disorder to order is compatible with this principle when the systems studied satisfy two very specific conditions. First the systems have to be open, which means that there has to be an exchange of matter and/or energy with the outside world. This condition releases from the law of increasing entropy and hence from the disorder imposed by the second principle of isolated systems."[c]

The theory of dissipative structures focuses on self-organizing phenomena, on the seemingly spontaneous emergence of an order, that is to say of a spatial and temporal morphology within a system made up of a great number of entities. In all cases, dissipative structures involve a "symmetry break". A homogenous, undifferentiated state

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[a] If cities obeyed the second principle of thermodynamics, like all closed systems, their entropy would grow in a continuous, irreversible manner. In other words, the system would tend to become uniform and singularities to dissolve. The state of maximal entropy, the state toward which all closed systems tend, is the most disorderly state, that is, the most undifferentiated possible state. The structure that results is called a structure in equilibrium.

[b] Ilya Prigogine, Isabelle Stengers, *La nouvelle alliance*, Paris, Gallimard, 1979, p. 198.

[c] Alain Boutot, *L'Invention des formes. Chaos, catastrophes, fractales, attracteurs étranges et structures dissipatives*, Editions Odile Jacob, 1993, p. 90-91.

(spatially and temporally) gives way to a heterogeneous, differentiated state that is less symmetrical than the prior one.[d]

Like in physics and like in semiotics, breaks of symmetry in cities create structure and meaning. Passeig de Gracia in Barcelona connects the original city that became the Barrio Gotico to the preexisting village of Gracia and is thus slightly shifted in the orthogonal grid of the city's extension without being a diagonal that would be integrated in the grid. It has been developed first in an astounding Art Nouveau Style. These 2 breaks of symmetry in space and in time have given Passeig de Gracia a central connective position and created a subtle large-scale order in the repetitive urban fabric of square blocks of Cerda's Eixample. The crossing of the 2 diagonals that Cerda intended to become the new center of the city did not break any symmetry and remained marginal compared to Passseig de Gracia.

1.3. Creative energy

Cities are not like stones or tables: they are not closed systems that can maintain their structure without exchanges of matter and energy with the outside. They are like candles whose flame burns steadily as a result of the disequilibrium in the energy flow that sustains it.

The disequilibrium of an urban system allows it to maintain a state of apparent equilibrium, that is to say, a state of stability and continuity. But this equilibrium can only break down if the system becomes self-enclosed. Seemingly closed Islamic cities of the past always had gates open onto the deserts, and the streets leading from the gates to the mosque were the very backbone of the urban structure. This was the case in the Islamic world but also in China where every city wall had its gates. The closed state is unstable and fragile, because it subjects the system to the second principle of thermodynamics, which states that all structures tend to dissipate in heat and disorder. On the other hand, in whirlpools, in flames, in our bodies, and in our cities, the openness allows the components to change within the structures, which remain stable, while slowly evolving.

The resilience of fractal structures is linked to their power to complexify so as to absorb fluctuations, to transform the waves of time into a constructive rather than a destructive force. The model in nature is the fractality that explains the geometry of coastlines. The energy of the ocean and the incessant movement of currents and waves that keep the coastal system far from equilibrium create a constant complexification by breaking the symmetry. In return, the increasingly complex coast absorbs the movement of waves and

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[d] Alain Boutot points out that Erwin Schrödinger (1887-1961) already expressed this idea. Schrödinger was trying to understand how living organisms, which are the very paragon of organized beings, maintain their organization despite Carnot's principle. "To explain this phenomenon, he formulated the following hypothesis: living organisms are open systems that avoid the thermal death predicted by the second law by constantly feeding on negative entropy."[d] "A living organism, according to Schrödinger, constantly increases its entropy – or one could say, creates positive entropy – and thus tends toward the dangerous state of maximal entropy, which is death. It can only hold it at bay, that is, stay alive, by continually extracting negative entropy from its environment." (E. Schrödinger, *Qu'est ce que la vie ?* Paris, Bourgois, 1986, p. 172).

dissipates its energy in an efficient way, self-limiting the process of erosion. We have here a natural example of non-dualist duality between form and energy where the dissipation of energy makes the forms more complex instead of destroying them and where this complexity ensures an optimal use of energy while increasing the resilience of the overall form/energy system.

2. Pareto distributions, scale free systems and urban optimization

The self-similarity of the parts and the whole can be summarized in a classical distribution in economy, the Pareto distribution, or inverse power law. The Pareto distribution relates the large, the intermediary and the small in measurable ways. It states that in a complex well-balanced system the frequency of an element of size x is proportional to the inverse of its size at an exponent m[e] characteristic of the system. In other terms there are few big elements, a medium number of medium-scale elements and a very large number (a "long tail") of small-scale elements, and the relative frequency of each type is determined by the mathematics of the Pareto distribution.

2.1. Pareto distribution and scale free structures

One of the main points for understanding the connection between the physical and topological structure of historical cities and their capacities of efficiency and resilience is the equivalence between fractal structure and the Pareto distribution.[f] By definition, a fractal structure has the property of scale invariance, which means that the distribution is the same on all scales. Mathematically this is written as $p(bx) = g(b) p(x)$. This functional equation is verified by any *p* fractal distribution. Its resolution is done simply by analytical methods, and leads to a unique category of solutions: $p(x) = kx^{-a}$, which is the exact definition of the Pareto distribution. This means that there is a mathematical equivalence between the Pareto distribution and the fractal distribution.

This long tail of Pareto distribution is at the origin of the most impressive business success stories of the Internet economy, such as Amazon. Instead of relying only on a few blockbusters (large elements sold by millions), Amazon has cut all the logistic costs of traditional distribution channels and made available to the world audience a long tail of millions of highly-differentiated products that even if sold at a few dozen samples each represent altogether a volume of sales much more higher than the blockbusters. It is full of lessons to see that highly successful agglomeration economies follow in their spatial organization the same patterns that the most successful businesses. The underlying reason is that economic efficiency and spatial efficiency are two different aspects of the

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[e] In spatial planning or in network design (street patterns, subways) this exponent can be interpreted under certain conditions as a fractal dimension, characteristic of the self- similarity properties of the system (it is generally around 1.2 for networks, between 1.6 and 1.85 for built footprints depending on the compactness of the city).

[f] Newman MEJ. "Power laws, Pareto distributions and Zipf's law," in *Contemporary Physics, 46:5*, 2000, pp. 323-331.

same coin: distribution efficiency in a highly differentiated world where exergy is maximized.

2.2. Exergy and emerging fractals

Industrial ecology,[g] as developed in particular by James J. Kay, provides a conceptual framework for understanding the sequence of local and global flows. The principle of industrial ecology is to use symbioses between the different components of a system to enhance its overall efficiency. This can easily be transposed to urban systems. In this framework, Kay proposes a thermodynamic approach based on the notion of exergy.

Exergy measures the maximum useful work that a system can draw from its available energy. Otherwise put, for a given quantity of available energy within the urban system, only a part, called exergy, is utilizable. The rest will be dissipated as heat during its transformation, thereby increasing the entropy of the system, without being useful in any way. For a given amount of energy, the bigger the exergy output, the more limited the increase of its entropy will be: the maxima of exergy output are also the minima of entropy output.

Extending Prigogine's considerations on open systems, Kay[h] shows that such a system pushed far away from thermodynamic equilibrium rejoins a stationary state of maximum exergy, that is to say, the optimal use of energy flows. This state corresponds exactly to the minimum of entropy production that Prigogine discusses. "An open system with exergy pumped into it is moved away from equilibrium, but nature resists movement away from equilibrium [...]. When the input of exergy and material pushes the system beyond a critical distance from equilibrium, the open system responds with the spontaneous emergence of new, reconfigured organized behaviour that uses the exergy to build, organize and maintain its new structure."[i]

Kay's work shows that a highly organized and highly structured system will utilize energy more efficiently than a more disordered system. A question remains: What is the best structure to give a city to maximize its efficiency as a system? The answer given by thermodynamics and Bejan's constructal theory is a fractal hierarchization, organized according to the Pareto distribution.

Bejan's constructal law[j] posits that for a flow-driven system to live and grow it must develop in a way that provides easy access to the flows running through it. Now, for systems subjected to certain types of flows, those that connect a point to a surface or a

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[g] Industrial ecology is a conception of industry that regards the industrial system as an ecosystem crossed by flows of material and energy.

[h] J.J. Kay, "On complexity theory, exergy and industrial ecology: some implications for construction ecology" in C. Kibert, J. Sendzimir & B. Guy, *Construction Ecology: Nature as the Basis for Green Buildings*, Spon Press, 2002, pp. 72-107.

[i] Ibid.

[j] A. Bejan and S. Lorente, "The constructal law of design and evolution in nature" in *Philosophical Transactions of the Royal Society B, 365*, pp. 1335-1347.

volume, Reis[k] has demonstrated the equivalence between the constructal law and the minimum entropy output predicted by Prigogine: the structures resulting from constructal theory are those that achieve the objective of maximizing exergy. For these flows, thermodynamics and constructal theory both describe the same optimal structure: a tree-like structure, with a main flow (the trunk) divided into secondary channels (the branches), which are subdivided into capillaries (twigs and leaves). Trees are fractal structures: they display the same pattern on every scale of branches dividing into smaller channels. This construction obeys scaling laws, that is to say the Pareto distribution.

2.3. Emergence

Emerging connective forces at all scales act on urban morphology to generate fractal structures. Emergence is the opposite of the utopian simplified orders that architects such as Le Corbusier have tried to impose on cities. Huge quantities of energy are needed in such artificial repetitive orders to maintain the urban system in a stable state. Modernist cities, with abstract giant forms imposed from the outside, obstruct the emergence of small-scale connections, whereas the continuous creation of connections in historical cities favored their evolution. The continuous fabric of traditional buildings with courtyards, because of its connective forces developing inwards, has a stabilizing impact on the urban system. Giant modernist buildings standing in loneliness isolation do not connect into the urban fabric. They have a destabilizing impact and fail to create an evolving adaptive structure. Modernist architects turned their back to the universal laws of urban evolution by working with large-scale elements only and making the urban land a blank slate devoid of the incremental successive layers of historical traces. The Utopian machinist juxtaposition of vast homogeneous zones, made of a repetition of very big objects, hinders the appearance of emerging properties that were not integrated or even forecasted or predictable into the initial framework of the system. For a property to emerge at a higher scale, smaller scales need to exist to foster its emergence. Each spatial scale supports the higher scales in the ascending hierarchy of an emergent complex order. These emergent properties allow the system to repair, stabilize itself and to evolve.

Emergent properties are analogous to the human brain. We cannot understand them by breaking down the system and analyzing its parts. Three conditions are needed for them to appear in a system: a high connectivity, the continuous creation of new connections and a sufficiently low degree of control, since lessening control implies increasing emergence, and vice versa.

The Internet and social networks, such as Facebook or Linkedin, are ceaselessly growing and increasing constantly their connectivity, while presenting scale-free properties in the structure of their connectivity that give order to myriad of data and allow us to navigate comfortably into them. Strikingly the street patterns of cities like the ancient town of

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[k] A. Heitor Reis, "Constructal Theory: From Engineering to Physics, and How Flow Systems Develop Shape and Structure," *Applied Mechanics Reviews*, 59, 2006, pp. 269-282.

Ahmedabad and Venice share the same connective structure as social networks when streets are considered as nodes of the network and links as relation between streets. This scale-free connectivity analogous to that of a leaf provides local efficiency of the network and a local clustering of short-range connections, without hindering global efficiency of the long-range connections.

A fundamental attribute shared by resilient living cities is a high degree of scale-free complexity. The geometric and topological assemblage of elements constitutes a series of organized wholes on each successive spatial scale and across the progression of scales. This fractal harmony is what distinguishes a coherent urban composition from the repetitive serial modernist utopias. Modernist cities are incapable of generating urban coherence. Geometric and topological coherence connects the city across all scales. It is crucial to the vitality of the urban fabric and to its exergy maximization.

In a fractal morphological field, the position and the form of each element are influenced by its interaction on different scales with all other elements. When the result of all these interactions creates a form, it is neither symmetrical nor fixed. It displays a degree of plasticity that allows it to evolve. Evolution is only possible if the large scale is correctly defined on the basis of a great many connections obeying a hierarchy of scale.

What matters more than the nature of urban elements is the structure of urban connections. In a multiply connected, living organic structure, the smaller components can be changed without affecting the overall structure. Building the whole from the parts in an organic way leaves room for evolution. Starting from the whole creates structures that cannot evolve. Modifying the urban whole once it has been established from a technical blueprint involves destroying a great many components on very different scales. In a bottom up city evolving through a myriad of micro processes, it is, to the contrary, easy to modify smaller components, like the arrangement of rooms in a house or the nature of buildings along a street.

The resilience of fractal street patterns derives from a network of paths that are topologically deformable. To be resilient, urban forms must not be defined once and for all. They must include degrees of freedom, be deformable and display a high degree of plasticity. They must be capable of accompanying the torsion, extensions and compressions of paths such as the ones that have occurred in Mediterranean cities after the fall of the Roman Empire, without tearing. To be deformable, the urban fabric must be strongly connected into the smaller scales and weakly connected into the large scale. This is a characteristic of the Japanese city with its multiplicity of short-range connections and average distances between intersections of around 50 meters in Tokyo as in Kyoto.

Deformability does not mean that the initial plan must be twisted and curvilinear. Orthogonal grids, be it in Kyoto derived from a Chinese imperial capital plan, in ancient Rome urban legacy around the Mediterranean, in the Latin American gridded plans of the XVIth century prescribed by *Las Leyes de las Indias*, have shown, provided they were originally enough fine grain, a remarkable propensity to evolve towards more complex

patterns. In India, the orthogonal legacy of the Hellenistic period has been filled by the fractal intricate patterns of Hindu cities and by the labyrinthine patterns of Islamic cities.

2.4. Interfaces and exergy maximization

The Pareto distribution and fractal structures associated with it have a unique capacity to ensure optimal efficiency of flows, which explains why they are so widely present in nature and in the structures that living organisms have selected as the most resilient over billions of years of evolution, and why they have been used to optimize industrial processes. Fractal structures are found in natural and artificial interfaces: pulmonary alveoli, plant roots, river basins, and electrodes in batteries. Large surfaces of interaction appear in fractal geometries. This is the case of systems in which either a physiological or an industrial process takes place through a membrane that must be optimized in a given volume. The geometric arrangement of alveoli in the lungs, for instance, has to be close to a fractal dimension of 3. Fractal interfaces display robust properties, which means that their performances are structural, formal, and less sensitive to variations in physical and chemical circumstances than other interfaces. This robustness explains why natural selection prefers living systems using this geometry. In cities, complex textures with courtyards and squares are what correspond to these porous membranes. Organized according to fractal scaling laws adapted to the climate, such textures optimize surfaces of heat, light, and energy exchanges, as a function of the city's bioclimatic parameters.

Thus the Pareto distribution is the universal starting point of efficiency optimization. Whether we are dealing with energy networks, flow systems, or urban textures, it alone ensures the maximization of exergy that this optimization requires.

2.5. Self-organization, long fluctuations, and catastrophes

Fractal structures optimize urban flows and are also vital in giving cities the resilience that they are lacking today. The more structured and complex the city, the more readily it can absorb the perturbations to which it is subjected, without letting them upset the stability of its structure. It is in assimilating the fluctuations and tensions that it complexifies. Hence, there is an ongoing dialogue between the city's capacities of resilience and the constraints to which it is subjected, between the fluctuations from the outside environment and its resistance to these fluctuations.

The resilience of a city is intrinsically linked to its self-organizing capacities. But self-organization is inevitably lodged in time, and the long span of natural fluctuations is not that of contemporary cities; the latter are designed and built very rapidly by authoritarian, rigid forms of urban planning..

Alongside long fluctuations, whose effects over centuries are sometimes imperceptible, there are short-term, even catastrophic fluctuations, which are becoming more frequent today, with their share of deaths and destructions. Cities were always subjected to them.

Cases in point are the Great Fire of London in 1666 and the earthquake in Lisbon that outraged Voltaire. But London and Lisbon both managed to live through these disasters and maintain their form, whereas contemporary cities are more and more vulnerable to earthquakes, droughts, floods, and natural and energy crises. They are vulnerable, to begin with, due to their low efficiency, and their voracity in energy and resources. They are also vulnerable because they are not adapted to their sites, to the environment they inhabit all in the same way and which, from one day to the next, may violently remind them of its existence and its identity, like the Chao Phraya delta into which Bangkok is inexorably sinking. Finally, they are vulnerable because of the disordered uniformity of their urban fabric, its absence of fractal structure, of scale free connectivity based on a long history that forges a city's capacities of resilience.

3. Arborescence versus leaf structures

Counteracting the vulnerability of contemporary cities requires a real paradigm reversal, and a shift from a mono-scale conception to a fractal conception of cities. Only fractal structures in the case of flow networks can secure optimal efficiency, while limiting the propagation of local perturbations. But another parameter is just as fundamental for the capacities of resilience of cities, and that is the fine-grained connectivity of their subjacent structures. This parameter entails pushing our thinking beyond the tree-like structures prescribed by simple thermodynamic considerations.

3.1. From trees to leaves

An arborescence is a highly hierarchic structure, and this hierarchization is precisely what causes its efficiency. This then is the first element we are seeking for the sustainable structure of the urban system: a strong scale hierarchy ensuring system efficiency. However, the connectivity of a tree is low: between two points there is only one possible path. For a city to be connected, it must be structured not like a tree but like a leaf.

A series of connections whose intensity obeys a Pareto distribution increases resilience by preventing rapid and catastrophic fluctuations from spreading quickly through the system and disorganizing it. There should be few long-range connections and these connections should be weak to prevent the spread of disrupting fluctuations. Weak connections are what allow the fluctuations to be absorbed. On the other hand, a great many strong short-range connections ensure the system's deformability. If efficiency is linked to the arborescence of elements, resilience is linked to a more abstract arborescence, that of the system of connections between elements the intensities of which should also obey a Pareto distribution.

As Alexander has noted,[i] one can readily see that street networks are not structured like trees: small streets are more often linked to one another or to several higher level streets,

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[i] Christopher Alexander, "A City is not a Tree" in *Design, 206*, 1965, pp. 46-55.

which is not the case in a tree structure. In fact, the underlying structure of these networks is what is called a "semilattice". A striking image of this type of structure is the system of veins on the leaves of most deciduous trees. Their leaves manifest a remarkable exception to the many tree-like systems observed elsewhere in nature. They display the same scale hierarchy, which proves again the universality of the Pareto distribution, but the midsize veins and the venules connect to one another, like the streets of a city, and so the connectivity is much stronger than in a tree-like structure.

3.2. Efficiency and resilience in semi lattice structures

The multiple connectivity and scale hierarchy that leaves and cities have in common enhance both their efficiency and their resilience.

Firstly, the loops that these structures contain, as Francis Corson has demonstrated,[m] manage variable flows more efficiently. The tree structure is most efficient when it comes to distributing stationary flows. But one of the characteristic features of urban flows is their extreme variability, both in time and in space. The semilattice structure absorbs these variations by distributing flows along different possible paths. This is impossible in a tree-like structure, where there is only one path between two points.

Secondly, the semilattice structure imparts greater resilience to a network. When a branch of a tree is cut, all those that grew from it will die too. In a leaf, if a vein is interrupted, the redundancy of the network will allow the flow to get around the interruption via secondary paths, so that it will only be partly slowed down by the degradation of the network. This is why cities structured like leaves are more resilient. Just imagine that a path is blocked by an accident: the flow is simply deviated onto other paths to irrigate the side beyond the perturbation. A part of the leaf's network can be amputated and the leaf will go on living and converting light energy into nutrients. Thanks to the scale invariance of the Pareto distribution, nature has provided for redundancy on all scales to ensure the permanence of its structures. The simultaneous existence of small and big nervures having the same function contains a natural redundancy for living organisms that answers the objective of efficiency and resilience with an economy of volume.

4. Superblocks: the super exponential collapse of connectivity and the violation of exergy laws

Historical cities have acquired over time a scale-free, multi-connected structure, like that of a leaf – a semi-lattice fractal structure. This structure connects and weaves the fabric of historical space. It contains small, narrow streets that connect to longer and wider streets that are themselves connected a few wide boulevards. This hierarchy results from the way

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[m] Francis Corson, "Fluctuations and redundancy in optimal transport networks," *Physical Review Letters, 104*, 2010.

in which such open systems far from equilibrium like cities are organized in reaction to the fluctuations of flows that run through them.

Quite the opposite, modernist cities, the archetype of which is Le Corbusier's *Radiant City*, do not provide fractal optimization. They are developed on one scale only, an inhuman scale of monotonous repetition of residential units and highways that distends and denatures the urban fabric. In contrast,

4.1. Superblocks and small blocks: sizing/scaling and differentiating

The highly complex leaf of Chinese traditional urban form has been almost completely erased during the last 30 years to be replaced by modernist cities organized by giant and simplified car oriented infrastructures. It is striking to see the correlation between the Chinese superblocks, mass developed during the last 30 years, and the under development in terms of linear density of an increasingly distended and disconnected street network, which, despite its gigantism, fails to organize and integrate the city into a real urban fabric. The gigantic scale of the roads in Chinese cities with their giant grid of 500 meters, and the very large mesh of subways with 1.5 km between stations, channel all the flows into a few constrained large arteries. The overall connective system lacks scale-free hierarchy with a differentiation of streets according to width, span and speed. It lacks topological hierarchy and clustering around hubs. This lack of hierarchy, alternative paths and clustering, ends up in severe local and global structural inefficiencies provoking congestion. Traffic problems are made even worse by the giant dead-ends that high towers are.

Chinese urbanization for the last 30 years has been based on these superblocks and giant infrastructures. The basic unit of development has not been the highly differentiated small block of historical Chinese cities or of European and American cities cores such as Manhattan, Boston, San Francisco, and Chicago. It has been the superblock of Le Corbusier modernist theories developed one century ago around 1920 and since then strongly criticized and abandoned in Europe and the U.S.

These superblocks are oversized: 400 meters to 500 meters side (and up to 800 meters side in some districts North of Beijing) to be compared to the very small block of Tokyo (50 meters side), of the Roman city and its legacy in Italian towns and most towns around the Mediterranean (70 meters side), of Paris, London and Manhattan (120 meters side). In terms of surface one 400 meters Chinese superblock (the most usual basic unit of panning of Chinese recent developments) equals 64 Japanese blocks. It equals 32 Mediterranean Europe blocks, and 11 Manhattan, Paris, London or Hong Kong blocks.

Inside superblocks, lack of diversity is provoked by the serial repetition of the same type of buildings usually on a dozen or even several dozen of superblocks and by the lack of subdivision in plots of the superblock. By contrast Manhattan small blocks were subdivided in the original plan of the city into dozens of plots with a differentiation according to the orientation (plots along the North-South avenues had not the same size

and geometry than the plots along the East-West streets) in order to encourage a specialization (businesses along the avenues and houses along the streets). The unit of development of Manhattan, London, and Paris has been the plot of about 500 m^2, each plot being developed differently by different economic actors. Thus the scale difference in the unit of city development between the Chinese superblock and the Manhattan plot is 320 fold and rises to about 3000 fold when a single developer develops 9 superblocks. The spatial land structure of Chinese contemporary developments is simply not fine grained enough to foster high levels of differentiation like in Manhattan or London.

To achieve differentiation, large and medium scale projects are of course necessary; but a long tail of small projects must complement them. In Manhattan it is possible to have on an area of 1.5 km2 (9 Chinese superblocks) a potential of 3000 different investors developing the urban fabric and the economic activities when in China a single developer develops a large scale mega project or a gated community in 9 superblocks. In Tokyo, where the plots are even smaller, the potential of differentiation and thus of resilience and adaptation, through the action of individual investors, raises 5000 fold above Chinese current practice. This highly differentiated urban fabric is at the same time more resilient and adaptive to changes (gradual or sudden). Differentiation potential is key to resilience and evolution. An undifferentiated system with only big elements, even if it covers a large territory, is only a small system inflated and its resilience and adaptive potential collapses compared to a really large system in terms of high differentiation and high number of structured interactions.

As with the 3000-fold collapse of differentiation potential, one may wonder if a collateral even stronger collapse in connectivity could not make Chinese recent development extremely weak in terms of resilience. An oversized urban fabric based on superblocks development with 3000 times less differentiation and an even stronger collapse of connections, compared with the small block urban fabric, may be equivalent structurally to a much smaller city and thus be unable to support the weight of a its mass of inhabitants. Superblocks are indeed shrinking Chinese cities when we look at them in terms of resilience. There is simply not enough structure in them to support their mass and channel their huge flows efficiently.

4.2. Superblocks and small blocks: connecting

The average distance between intersections is a good indication of the grain of a city. The grain of new Chinese cities (500m between intersections in average in new developments) is 7-fold coarser than the grain of Turin, Italy (70m between intersections in average), and more generally of most European or Japanese historical urban cores. There is a 4-fold increase between the grain of Paris/London/Manhattan (around 125m between intersections in average) and the grain of Beijing new developments (500m between intersections in average).

In terms of connectivity, this translates in a simplified model, comparing 100km² urban

areas:

	Paris/London/Manhattan	Tokyo/Kyoto	Beijing
Number of blocks	6,400	40,000	400
Number of intersections	6,400	40,000	400

When comparing the number of intersections and blocks in Beijing and international cities, the difference is 100-fold with Japan, 16-fold with Europe and Manhattan. The grain of the city directly impacts on the number of available paths in the city. High numbers of possible paths avoid congestion effects in the network and increase its resilience, by providing many alternatives to go from one point to another within the city.

The number of possible paths between two locations in the city is directly related to the number of links between intersections, and is gigantic. As people act in a rational way, they tend to use the shortest path. In the following example, a person wants to travel from point A to point B in a theoretical grid of side n. Using the following grid, the distance between A and B is 2n. The number of available paths in this grid is equal to $(2n)!/(n!)^2$, that grows exponentially with n.
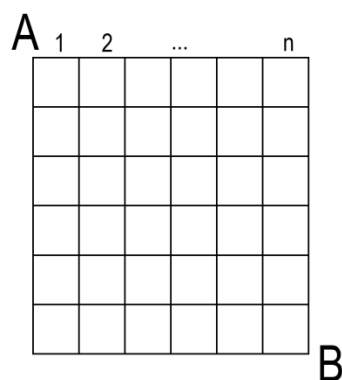
Let us now compare Beijing, Paris and Tokyo on a 1km² area, point A and point B being in the opposite corners. With an average distance of 500 meters between intersections, the street network in Beijing displays in average 3 intersections for 1km. n equals 3. The number of possible paths is $6!/(3!)^2$, that is 20. With an average distance of 125 meters between intersections, the Parisian street network displays 5 intersections for 1km. n equals 5. The number of possible paths is $10!/(5!)^2$, that is 252 paths. With an average distance of 50 meters between intersections, the street network in Tokyo displays in average of 20 intersections for 1km. n equals 20. The number of possible paths is $40!/(20!)^2$, that is more than 100 billion paths!

Empirical measurements show this phenomenon on real fabric samples. They show the connectivity potential of fine grain cities like Paris or Manhattan, or of super fine grain cities such as Tokyo, which explains their resilience. To give an idea of the exponential growth of the connectivity potential: on just a square km shifting in Beijing the grain from 500 m side to 125 m side would lead to an increase of the potential paths from 20 to 252.

This abstract simplified model, which is based on the real empirical differences between Paris/London/Manhattan grain, Tokyo/Kyoto grain and Beijing grain, shows that sizing/scaling is dual to connecting and that shifting towards finer grain has exponential effects in increasing the links and thus the interactions necessary to increase the resilience of urban structures and their efficiency in maximizing exergy.

5. Connecting, differentiating and the maximization of exergy

5.1. A tale of three cities

Three highly successful resilient cities, London, Manhattan, Tokyo, have a highly connected and highly differentiated at all scales city structure.

Manhattan grid (avenues and streets), block sizing, and parcels sizing differ according to orientation and this seems to be the minimal conditions in order to create an enormous potential of differentiation. At the global Manhattan scale, the historical preexistence of New Amsterdam (now Wall Street) at the bottom part of the city, the diagonal of Broadway (a former Indian path way), the creation of Central Park are certainly the main seeds that have pushed to the emergence of socially, functionally and even stylistically highly differentiated neighborhoods from the rather uniform Commissioners' plan of 1811. The urban fabric (physical and social) of Wall Street is totally different from the one in Soho or Tribeca or from the one in Upper East Side. Manhattan has been the receptacle of massive immigration influx from Europe and has evolved (and is still evolving) for two centuries with a constant increase in the complexity of its structure and in its differentiation. Manhattan is a fine grain "planned" city only in the design of its street patterns and of its land division into parcels. Myriads of individual initiatives have then shaped the evolving form of the city. The city results from a delicate balance of overall planning giving an overall stable and fine grain framework to a myriad of market forces.

In contrast, London is not a city planned from the beginning. It is complex, connected, and highly differentiated while being integrated. Its urban form results from a balance between history and market forces. The land division into parcels has maintained the historical continuity of the most ancient parts (and now the most modern, vibrant and bustling of economic activity) of the city. Due to the stubborn resistance of London inhabitants to planners' intentions to rebuild the city according to a "rational" orthogonal grid after the Great Fire of 1666, the city has kept in its central part, one of the most powerful financial centers in the world, its medieval street patterns. In contrast Lisbon after the earthquake of the XVIIIth century has been rebuilt according to an orthogonal grid.

Tokyo is different from both Manhattan and London. It has been shaped by topography, the differentiation created by the "empty" Imperial palace in the center, and the spiraling movement of different neighborhoods around this invisible, sacred and empty core. The Shogun original intention was to build for him a capital according to an orthogonal

geomantic model like the series of Japanese Imperial capitals derived from the Chinese model. Tokyo now is a gigantic mosaic of mostly low rise and very fine grain different neighborhoods that give to their inhabitants a strong local human scale while being integrated into a whole that despite its gigantic, physical and human, scale manifests a kind of complex integrated order. With its 37 million inhabitants, Tokyo, the largest city in the world since 1980, has succeeded to create a subtle order and sense of place both at the very local and at the very global scale.

5.2. Five strategies for fostering the emergence of exergy efficient urban structures

Despite their differences, what is common in London, Manhattan, Tokyo, three resilient cities that have lasted centuries and have all succeeded to be the economic dominant world city at different moments in history? Can we find in their urban form common features that explain why they have been extremely resilient, have organized the planet around them and have derived the maximum benefits of agglomeration economies? In return, how market forces have shaped them in the sense of a successful differentiation? What lessons can we derive from their success, to define strategies for increasing the resilience of cities?

5.2.1. Wholeness

These three cities are extremely complex wholes that present a pervasive and elusive sense of unity and uniqueness. Despite their extreme diversity, they have an immediately recognizable unity: you cannot mistake Tokyo with London or Manhattan and even with another Japanese city like Osaka. At all scales (street, neighborhood, district, city) they provide a sense of belonging to an identifiable whole. Each scale is well defined and smoothly integrated to the upper scales, delivering constantly through the different scales a strong sense of place.

5.2.2. Diversity

The amount of diversity inside this complex unity is enormous. This diversity has been created by history and by myriads of different sizes initiatives along a long period of time. Not a single brownstone house is exactly identical to the other in Manhattan Upper East Side. Along Central park on Fifth Avenue, the Museum mile and the wealthy mansions stand in strong contrast to the quieter inside the street brownstone houses.

5.2.3. The "signature" of complexity

The relations between the human scale and the city scale, between the diversity and the unity, between the local and the global, between the "small" and the "large", between the

"units" and the "whole", are not random relations. They show the "signature" of complexity, that is the typical structure of complex systems that have evolved for billions of years like life or just for decades like the internet and social networks and have survived, prospered and colonized the Earth thanks to their high efficiency, resilience and adaptive qualities. All these complex structures, organic or artificial and man made, share the same property: they are scale free, meaning that when we look at them at different scales they show the same amount of complexity and structure. When we look at a district in Paris or Manhattan, for example, we find the same relative distribution of large public parks, medium scale and pocket parks smaller than half hectare, than in the whole city. Each district is a reduced scale version of the city for the relative distribution of sizes of amenities such as public parks, health, education, and shops. When we look at the distribution of sizes of streets in Paris, we find at city scale and at district scale the same blend of 20 meters wide boulevards, 12 meters wide streets, 10 meters wide, 8 meters wide. Each sub pattern of streets at neighborhood and district scales presents the same distribution properties as the whole city.

5.2.4. Connectedness

All three cities are extremely well connected at all intra-urban scales. This connectivity also is not random connectivity: it exhibits properties of highly efficient networks. Here again a structure emerges that unites many different fields from economy to engineering to social networks. This structure is scale free in the structure of its relations. In a network, what is even more important than geometry is topology, that is the structure of relations.

Networks can be described as nodes (for example subway stations or people on Facebook in a social network) and links between nodes. The degree of a node is its number of its links, for example the number of links between a subway station and its neighboring stations, the number of your friends on Facebook or Linkedin.

Here the analogy between the networks of our three successful cities is with the success of social networks. A social network like Facebook is scale free: any sub-network at all scales has the same structure as the whole network. For example the sub-network of people living in Soho shows the same structure as the sub-network of Manhattan, which shows the same structure as the sub-network of New York, which shows the same structure as the sub-network of the East Coast, which shows the same structure as the sub-network of the U.S., which shows the same structure as the sub-network of the world Facebook.

Social networks as well as street networks in complex evolved cities show other interesting characteristics that are summarized in the term of "small world" properties. In particular they show a high level of clustering, meaning that neighboring nodes are also linked in a high proportion. In simple terms, clustering means that there is a high probability that your friends on Linkedin be friends or become friends in between themselves, creating a "small world" that is in return connected by hubs to other "small

worlds". This property has made the success of social networks on the Internet and interestingly is the way airlines have organized the traffic with continental hubs to minimize their cost and maximize their routes and economic efficiency. It can be shown that complex evolved street patterns show this small world property when a street is considered as a node and its intersection with another street as a link. Complex subway systems, such as the ones in Tokyo, London, Manhattan, tend to evolve with a long time and multiple decisions towards the same structure as social networks. From the "small world" properties a number of measures of efficiency can be derived such as characteristic path length, global and local efficiencies.

5.2.5.   Continuity at human scale

Fifth, all three cities show local human scale, made of continuity and closeness of a fine grain built urban fabric, diversified in its functions, with a well-sized and continuous public space. Density matters but Manhattan, London and Tokyo show different built densities from high in Manhattan (although not significantly higher than 7 floor high Paris despite some vertical parts) to medium in London, and in most parts of Tokyo made of a continuous fabric of small 2 floor individual houses. Verticality is not density and interestingly even a city where verticality is very well planned in a fine mesh of 30 meters wide avenues and 20 meters wide streets has a demographic density almost identical to that of Paris (24 000 people/m^2) and only 50% higher than that of Seoul or Tokyo. Yet what matters more than density and is common to these cities is continuity, fine grain diversity and human scale.

6.   Conclusion: A city is not a machine

By their openness to the environment and the productive disequilibrium created by the incessant activity of people and transformations of societies, cities exhibit a profoundly different nature and logic than machines. Cities are not artefacts; they are living organisms that are born, grow, age, and die. The organization of cities cannot be understood from the same perspective as artificial machines. Cities, like life itself, but unlike machines, have an aptitude to create complexity according to a much more complex logic than that of an artificial machine. At the heart of this ability is the phenomenon of self-organization[n] provoked by exergy maximization in an open system far from the equilibrium.This phenomenon accounts for the adaptive capacities of life and cities.

"The *artefact* machine components are extremely reliable," Edgar Morin writes, "but the machine as a whole is much less reliable than its individual components. All it takes is an

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[n] The theory of self-organization has two starting points: firstly, Schrödinger in 1945 set forward the paradox of the organization of living systems that does not seem to conform to the law of thermodynamics alone; next, Von Neumann lodged the paradox in the difference between living (self-organizing) machines and artificial (simply organized) machines or *artefacts.*

alteration in one of its components for the system as a whole to block and break down, and then it can only be repaired by external intervention. In contrast, the components of the living (self-organizing) machine are not very reliable because molecules degrade very quickly, and all organs are, of course, made of molecules; moreover, in an organism, molecules, like cells, die and are renewed, but the organism remains identical to itself, even when all its components have been renewed. So in diametrical opposition to the artificial machine, the system is reliable while its components are not."[o]

Cities share the self-organizing character of living organisms. Just look at the way Rome morphed from a Roman grid over the course of two thousand five hundred years to see the extent to which a city can be at once the same and different, and recreate the material and in part the form of all its elements over time.

Self-organization also shows that there is a *consubstantial relationship between disorganization and complex organization*. To quote Edgar Morin again, "the phenomenon of disorganization (entropy) continues its course in the living, even more rapidly than in the artificial machine, but it is inseparable from the phenomenon of organization (negentropy). This then is the fundamental link between entropy and negentropy, which are by no means two opposing entities. In other words, there is a much closer, deeper link between life and death than metaphysics ever imagined."[p]

The entropy of cities tends to ruin their organization, but paradoxically they can only grow and become more complex in an organic way out of disorder, or rather, to borrow Von Foester's term, out of the "noise" in the information. This paradoxical basis of self-organization is absolutely general and cities are but a particular example of living systems. Thus, ignoring or repressing the element of disorder and spontaneity in urban life, and replacing it, as Le Corbusier did, by a mechanistic view, frozen for all eternity, amounts to condemning the city to the death of artefacts, for nothing lives that is not constantly dying to renew itself.

Bibliographical references

[1]. Albert, R., Jeong, H. & Barabási, A., 2000. "Error and attack tolerance in complex networks". Nature 406, 378.
[2]. Alexander, C., 1965. "A city is not a tree". Design, Volume 206, pp. 46-55.
[3]. Bejan, A. & Lorente, S., 2010. "The constructal law of design and evolution in nature". Philosophical transactions of the Royal Society B, Volume 365, pp. 1335-1347.
[4]. Buhl, J. et al., 2006. "Topological patterns in street networks of self-organized urban settlements". The European physical journal B 49, p. 513–522.
[5]. Buhl, J. et al., 2004. "Efficiency and robustness in ant networks of galleries". The European physical journal B, 42, pp. 123- 9.
[6]. Corson, F., 2010. "Fluctuations and redundancy in optimal transport networks". Physical Review Letters, 29 January, Volume 104.
[7]. Dawkins, R., 1986. *The blind watchmaker*. Longman Scientific and Technical.
[8]. Dunne, J., Williams, R. & Martinez, N., 2002. "Food-web structure and network theory: The role of connectance and size". PNAS 99.

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[o] Edgar Morin, *Introduction à la pensée complexe*, 1990, p. 43-44.
[p] Ibid.

[9]. Edelman, G. & Tononi, G., 2000. *A Universe of Consciousness.* New York: basic books.

[10]. Heitor Reis, A., 2006. Constructal "Theory: From Engineering to Physics, and How Flow Systems Develop Shape and Structure". Applied Mechanics Reviews, Volume 59, pp. 269-282.

[11]. Holme, P., Kim, B., Yoon, C. & Han, S., 2002. "Attack vulnerability of complex networks". Phys Rev E Stat Nonlin Soft Matter Phys. 65.

[12]. Kay, J., 2002. *On complexity theory, exergy and industrial ecology: some implications for construction ecology.* Spon Press.

[13]. Latora, V. & Marchiori, M., 2003. "Economic small-world behavior in weighted networks". The European Physical Journal B, 32, pp. 249-63.

[14]. Newman, M., 2002. "Assortative mixing in networks". Phys. Rev. Lett. 89.

[15]. Newman, M., 2005. "Power laws, Pareto distributions and Zipf's law". Contemporary Physics, May, 46(5), pp. 323-3351.

[16]. Rossi, A., 1981. *L'architecture de la ville.* Paris: L'équerre.

[17]. Salat, S., 2011. *Cities and Forms, On Sustainable Urbanism*, Paris, Hermann, Beijing, China Architecture and Building Press.

[18]. Salat, S. & Bourdic, L., 2011. "Scale Hierarchy, Exergy Maximisation and Urban Efficiency". ELCAS2, Nisyros.

[19]. Salingaros, N., 1998. "The theory of urban web". Journal of Urban Design, 3, pp. 53-71.

[20]. Simon, H., 1962. "The architecture of complexity". Proceedings of the American Philosophical Society, 106(6), pp. 467-82.

[21]. Tannier, C., 2009. "Formes de cités optimales, formes de cités durables. Réflexions à partir de l'étude de la ville fractale". Espaces et Sociétés, 3(138), pp. 153-71.

[22]. Vance, J., 1990. *The continuing city: Urban morphology in western civilization.* Baltimore & London.

[23]. Brenner, N. (2009), "A Thousand Leaves: Notes on the Geography of Uneven Spatial Development", in Keil, R., Mahon, R. (eds.), *Leviathan Undone? Towards a Political Economy of Scale*, UBC Press, Vancouver.

[24]. Brunet, R. (1996), "L'Europa delle reti", Memorie geografiche, n. 2, Società di Studi Geografici, Firenze.

[25]. Castells, M. (1996), *The Rise of the Network Society, The Information Age: Economy, Society and Culture*, Vol. I, Blackwell, Oxford - Cambridge.

ON THE PRINCIPLES/IMPORTANCE OF THERMODYNAMICS

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1. Introduction

Precise thermodynamics education is a requirement to discuss issues that one faces in thermodynamics and resulting studies in global warming, energy conversion and other energy related topics that affect sustainability of the environment in the global sense. For this reason, learning, understanding and meaningful and relevant application of topics in thermodynamics are required.   To accomplish this, educating students at the undergraduate and graduate levels in classical, statistical and non-equilibrium thermodynamics becomes important. Here a short synopsis of fundamentals of classical thermodynamics are discussed with the intent of bringing clarity to the laws of thermodynamics and their application in design of experiments, applications in other fields such as heat transfer, and physical interpretation of the mathematical relations that are so useful in explaining why certain things happen in thermodynamics and nature. Nature is the ultimate customer.

For all scientist and engineers, the courses that end in –ics must be studied and understood well with their correct and precise application, such as mathematics, physics, chemical kinetics, mechanics as well as ethics and economics.   Of course, thermodynamics is one portion of mechanics that is very important in the education of all engineers.. It relates natural phenomena to some order and disorder. From a thermal energy point of view therefore, thermodynamics is the science that dictates what happens in nature and what not and why. Thus to better understand nature, the implications of energy usage on the environment and sustainability of what we enjoy today, we need to study precise thermodynamics.

2. Definitions

Definitions in thermodynamics must be precise to make everything that follows correct. Thus, in nature, there are only three types of systems. The closed system is one for which the mass within the boundaries remain a constant, such as a tank or a piston-cylinder arrangement. The filling/emptying system is the one that a tank with a valve characterizes where mass can *either* enter *or* leave the tank.   Both cannot occur simultaneously. If a system has mass entering and leaving the boundaries, then it is called open.

There are only eight thermodynamic properties. The measurable ones are pressure, p, volume, V, and temperature, T. As a consequence of the first law of thermodynamics,

internal energy, U, is introduced followed by the second law of thermodynamics and the introduction of entropy, S. Then three convenience properties are defined in terms of the five above: enthalpy H = U+pV, the Gibbs' function G = H-TS, and the Helmholtz potential F = U-TS. The rest should be called physical properties of a system, such as the mass m.

In thermodynamics equilibrium is required to solve a problem. By definition, when two systems reach the same temperature T, they are called to be in thermal equilibrium. When they reach the same pressure p, they have mechanical equilibrium, and when they have the same electrochemical potential μ_i , they have chemical equilibrium. When all three happen simultaneously, then thermodynamic equilibrium exists.

One of the more important statements in thermodynamics is the state principle. This principle is important not only in thermodynamic analyses but in applied areas like heat transfer. This principle states that any two independent and intensive thermodynamic properties would define any of the others and fix a thermodynamic state and the situation is unique no matter which choice is made. A lack of understanding of this principle may lead into published work which has no meaning at all, Chawla (1978). Thus once a thermodynamic state is defined then a characteristic line that connects any two such states is called a thermodynamic process. A sequence of thermodynamic processes ending up at the initial thermodynamic state is called a thermodynamic cycle.

3. Conservation equations

These equations that apply may be obtained using the Reynolds' Transport Theorem. Its use is common to all of these conservation laws and will be done systematically for each one of them. Considering at time t, $B_{system}(t) = B_{CV}(t)$ and at time t+Δt, $B_{system}(t+\Delta t) = [B_{CV}(t+\Delta t) + B_{out} - B_{in}]$ where the amount of B that exited the control volume is given as $B_{out} = b(m_{out}) = b[(\rho)(\vec{V}_{out})(A_{out})(\Delta t)]$ and $B_{in} = b(m_{in}) = b[(\rho)(\vec{V}_{in})(A_{in})(\Delta t)]$ is the amount of B that entered the control volume. Subtracting the first term from the second and dividing by Δt results in

$$\frac{B_{system}(t + \Delta t) - B_{system}(t)}{\Delta t} = \frac{B_{CV}(t + \Delta t) - B_{CV}(t)}{\Delta t} + \frac{b[(\rho)(\vec{V}_{out})(A_{out})(\Delta t)] - b[(\rho)(\vec{V}_{in})(A_{in})(\Delta t)]}{\Delta t} .$$

Taking the limit of this equation as Δt approaches 0 yields the simplified equation

$$\frac{dB_{sys}}{dt} = \frac{dB_{CV}}{dt} + b\rho \left[\vec{V}_{out} A_{out} - \vec{V}_{in} A_{in} \right] .$$

Rewriting the outflow and inflow terms for the entire control surface in this equation gives

$$\frac{dB_{sys}}{dt} = \frac{dB_{CV}}{dt} + \int_{CS} \rho b \vec{V} \cdot \vec{n} dA$$

where the dot product, $\left(\vec{V} \cdot \vec{n}\right)$, is defined as (V n cosθ) where θ is the angle between $\vec{V}$ to $\vec{n}$. The total amount of extensive property B, (B=m b), in the control volume is

determined by integrating over the entire control volume as $B_{CV} = \int_{CV} \rho b dV$. Upon substitution and combination, the <u>Reynolds Transport Theorem</u> is obtained as

$$\frac{dB_{sys}}{dt} = \frac{d}{dt} \int_{CV} \rho b dV + \int_{CS} \rho b (\vec{V} \bullet \vec{n}) dA$$

where the left hand term is the time rate of change of extensive property (B) in the system, the first term on the right hand side of the equation is the time rate of change of intensive property (b) in the control volume, and the second term on the right hand side of the equation is the net flow of intensive property (b) across the control surface. A positive value indicates net flow across the control surface is out of the control volume while a negative value indicates net flow across the control surface is into the control volume.

There are two conservation equations, that of mass and energy – the first law of thermodynamics. For the case of conservation of mass,

Closed system: $m = $ constant.

Open system: $\sum_{in} \dot{m} = \sum_{out} \dot{m}$

Filling system: $m_{initial} + \sum_{in} m = m_{final}$

Emptying system: $m_{initial} - \sum_{out} m = m_{final}$.

Applying the Reynolds' Transport Theorem to the first law of thermodynamics, the result becomes $\frac{dE_{system}}{dt} = \frac{d}{dt} \int_{CV} \rho e dV + \int_{CS} \rho e (\vec{V} \bullet \vec{n}) dA$.

This statement is very similar to money and banking; the difference is that nature does not permit overdraw of funds, namely one cannot use what is not there, whereas the bank just charges us money for overdraft. At steady state, therefore, $\delta Q - \delta W = dU$. For a cycle, $\oint \delta Q = \oint \delta W$ resulting in the fact that $\oint dU = \oint d(property) = 0$. This is a very important result which will be used later. Application of the above theorem to various systems in nature results in the first law of thermodynamics as

Closed system: $Q_{ie} - W_{ie} = U_e - U_i$

Open system: $\dot{Q}_{ie} - \dot{W}_{ie} = \sum_{e} \dot{m}(h + \frac{\vec{V}^2}{2} + gz) - \sum_{i} \dot{m}(h + \frac{\vec{V}^2}{2} + gz)$

Filling system: $Q_{ie} - W_{ie} = m_2 u_2 - \sum_{i} m(h + \frac{\vec{V}^2}{2} + gz) - m_1 u_1$

Emitting system:
$$Q_{ie} - W_{ie} = \underset{e}{\Sigma} \, m(h + \frac{\vec{V}^2}{2} + gz) + m_2 u_2 - m_1 u_1$$

4. Sign convention in thermodynamics

We cannot overemphasize the importance of this since most, if not all, textbooks do not strictly follow the convention. What convention is followed is not important, the consistent use of it is. For example, Callen (1960) says that all energy in is positive and all energy out is negative, and in that text this is followed consistently whereas most commonly used undergraduate and graduate textbooks do not, as is shown in the Bibliography and References of Arnas, et al (2003). Precision is very important, as is mentioned in Obert (1960) In most textbooks, all energy transfer due to a difference of temperature only called heat, in is positive and heat out is negative, and all energy transfers due to a potential difference other than temperature called work, in is negative and work out is positive giving us HIP to WIN. In all that we will do, this convention will be followed due to its universal and more common usage. For the equivalence of heat to absolute temperature, consider a Carnot cycle, Fig.1. It is made of two reversible adiabatic lines and two constant temperature heat reservoirs. If the working fluid is considered to be an ideal gas, for simplicity of algebra, then the energy added at T_H is given by, for an ideal gas, $\left(Q_{bc} = \frac{m\mathfrak{R}}{M} T_H \ln \frac{V_c}{V_b} \right)$.
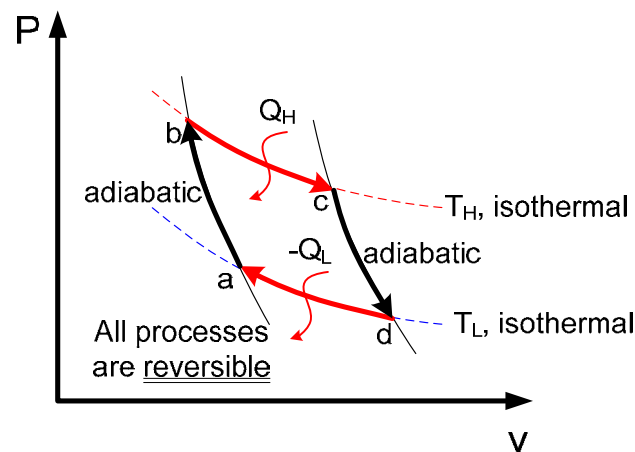

Fig: 1. The Carnot cycle

Similarly for the process (d-a), $\left(Q_{da} = \frac{m\mathfrak{R}}{M} T_L \ln \frac{V_a}{V_d} \right)$; thus the ratio becomes

$$\left[\frac{Q_{da}}{Q_{bc}} = \frac{T_L}{T_H} \left(\frac{\ln \frac{V_a}{V_d}}{\ln \frac{V_c}{V_b}} \right) \right].$$

Since the process (a-b) is reversible and adiabatic, then [- m c_v dT = p dV] = $\left[\dfrac{m\Re}{M} T \dfrac{dV}{V} \right]$.

This integrates to give for process (a-b) the result of $\left\{ -\dfrac{M}{\Re} \displaystyle\int_{T_L}^{T_H} c_v \dfrac{dT}{T} = \ln \dfrac{V_b}{V_a} \right\}$.

For the process (c-d), a similar results is obtained as $\left\{ -\dfrac{M}{\Re} \displaystyle\int_{T_H}^{T_L} c_v \dfrac{dT}{T} = \ln \dfrac{V_d}{V_c} \right\}$.

Therefore, since the limits of integration are reversed, the equivalence gives $\left\{ \ln \dfrac{V_a}{V_b} = \ln \dfrac{V_d}{V_c} \right\}$ or {-[ln V_c − ln V_b]} = [ln V_a − ln V_d] resulting in $\left(\ln \dfrac{V_c}{V_b} \right) / \left(\ln \dfrac{V_a}{V_d} \right) = -1$. This

upon substitution yields the expected result of $\left(\dfrac{-Q_L}{Q_H} = \dfrac{T_L}{T_H} \right)$.

This relation permits one to substitute temperatures for heat quantities in the determination of Carnot performance criteria which quickly give extremum values for the actual efficiencies for engines, η, as well as coefficient of performances for refrigerators, β, and heat pumps, γ. It must be remembered that one of the heat quantities is negative, out of a system, as it should be since the ratio of absolute temperatures is always positive. With reference to Arnas, et al (2003), we can examine the various details of this result particularly with respect to engine efficiency and refrigerator and heat pump coefficient of performances. For this demonstration, we will use the sign convention of Callen (1960) that all energy transfers into a system are positive and all out of the system are negative.

5. Performance characteristics of devices

Consider a heat engine that receives energy (Q_H) from a reservoir at (T_H) and produces work ($-W_{net}$) while rejecting energy ($-Q_L$) to a reservoir at (T_L). Since the performance of any device is measured by the ratio of the net useful effect to the total cost to obtain that

effect, then $\eta = \left(\dfrac{-W_{net}}{Q_H} \right)$. Also we have $\Sigma E_{in} = \Sigma E_{out}$ giving $Q_H = \left[-W_{net} + (-Q_L) \right]$.

Solving for $(-W_{net})$ and substituting into the efficiency equation, the result becomes

$$\eta = \left(\frac{Q_H + Q_L}{Q_H} \right) = \left(1 + \frac{Q_L}{Q_H} \right).$$

Using the equivalence equation, the efficiency of a Carnot engine reduces to

$$\eta = \left(1 - \frac{T_L}{T_H} \right).$$

For a refrigerator, the net effect is the cooling that we get, (Q_L), from a cold reservoir at (T_L). The work required to pump this energy is (W_{net}), and the energy given off to the environment at a temperature (T_H) is ($-Q_H$).   Therefore, the performance parameter, coefficient of performance for a refrigerator becomes

$$\beta = \left(\frac{Q_L}{W_{net}}\right) = \left[\frac{Q_L}{-Q_H + (-Q_L)}\right] = \frac{1}{\left(-\dfrac{Q_H}{Q_L} - 1\right)} \quad \text{which reduces to} \quad \beta = \left(\frac{T_L}{T_H - T_L}\right) \quad \text{for a}$$

Carnot refrigerator.

For a heat pump, the net effect is the heating that we get, ($-Q_H$) into a reservoir at a temperature of (T_H). The work required to pump this energy is (W_{net}), and the energy that is taken out of the environment at a temperature (T_L) is (Q_L). Therefore, the coefficient of performance for a heat pump becomes

$$\gamma = \left(\frac{-Q_H}{W_{net}}\right) = \left[\frac{-Q_H}{-Q_H + (-Q_L)}\right] = \frac{1}{\left(1 + \dfrac{Q_L}{Q_H}\right)} \quad \text{which reduces to}$$

$$\gamma = \left(\frac{T_H}{T_H - T_L}\right) \quad \text{for a Carnot heat pump. It is also easy to prove that } \{\gamma = (1 + \beta)\} \text{ using the}$$

results obtained above.

6.   Second law of thermodynamics

The second law of thermodynamics denies a system the possibility of utilizing energy in a particular or arbitrary way. There are two basic definitions of the second law which were stated at different times by different people, historically speaking.

Kelvin-Planck statement

It is impossible to construct an engine which is operating in a cycle that will produce no effect other than the extraction of energy from a reservoir and the performance of an equivalent amount of work. Thus an efficiency of 100% is not a possibility.

Clausius statement

It is impossible to construct a device which while operating in a cycle will produce no effect other than the transfer of energy from a colder to a hotter body. Thus a refrigeration unit requires energy input as work; otherwise it cannot function.

These two statements are equivalent and the assumption of the validity of one leads to the situation given by the other. Consider that the Kelvin-Planck statement is valid. If now one constructs a refrigerator running with the work of the engine and extracting energy [-

Q_c] from the cold reservoir, then the engine-refrigerator system is one which absorbs energy from a cold reservoir and transfers it to the hot reservoir without any external work, a situation which the Clausius statement refutes. If this were possible, the energy in the oceans at a low and cold temperature could be utilized to run all kinds of equipment without any external work; an impossible situation known to all.

If now the Clausius statement is considered to be valid, then the refrigerator functions without any external work. At the same time, an engine placed between the same two reservoirs produces work. The refrigerator-engine system leads to a situation where an amount of energy is absorbed from a hot reservoir and an equivalent amount of work is performed, a situation that the Kelvin-Planck statement refutes. If this were valid, all the fuel consumed in the engine of a car would be used in the form of work without any losses whatsoever; another impossible situation that is well known to all. All physical systems must function in such a way as not to violate either one of these statements. Otherwise a perpetual motion machine of the second kind will result.

7. The CARNOT Principle

This is one of the fundamental principles of thermodynamics. It says that there is no heat engine operating between two given reservoirs that can be more efficient than a Carnot heat engine operating between the same two reservoirs. To prove this statement, assume that the reverse is true. Then since the Carnot engine is reversible, it can be reversed to operate as a refrigerator. Therefore, if the engine E is more efficient than the Carnot engine CE, the result becomes ($\eta_E > \eta_{CE}$).
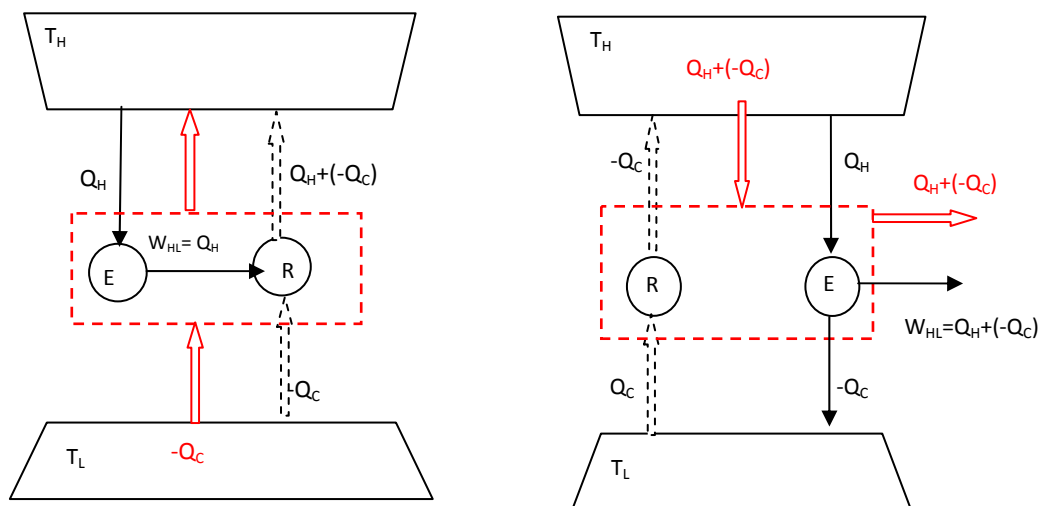

Fig: 2. The graphical explanation of the Kelvin-Planck and Clausius statements of the second law.

This can also be written as $\left(\dfrac{W}{Q_H} > \dfrac{W}{Q_C} \right)$ giving as the final result $\left(Q_C > Q_H \right)$. If this is

the case, then there is a net flow of energy in the form of heat from the cold to the hot reservoir without any consumption of work or other external effects. Such a result is impossible since it leads to the contradiction of the Clausius statement of the second law of thermodynamics. Thus the original assumption was wrong which says that the efficiency of an engine cannot be larger than that of a Carnot engine operating between the same two reservoirs. A corollary to the Carnot principle is that all Carnot engines operating between the same two temperature reservoirs T_H and T_L have the same efficiency. The proof of this statement follows from the above. Assume that the first one is more efficient than the other. A contradiction will be observed. Then assume the other way around. The same contradiction will be obtained. The only possibility remaining, therefore, is naturally the equivalence of the two efficiencies.

8. Entropy

Entropy is a thermodynamic property which comes about as a result of the second law of thermodynamics. To demonstrate its existence, following Zemansky (1943) and Mooney (1953), consider a reversible process from an initial state i to a final state f and use the first law to give $\left[Q_{if} - W_{if} = \left(U_f - U_i \right) \right]$, Fig. 3. From i and f draw two reversible adiabatic lines. Then construct a reversible isotherm (a-b) so that the area above and below the isotherm and between the original process (i-f) and the adiabatic lines are equal. Thus, we obtain that $\left(W_{if} = W_{iabf} \right)$.

Therefore, now the heat terms give $\left(Q_{if} = Q_{iabf} \right)$ since ($U_f - U_i$) does not change because of the general character of a thermodynamic property. Also Q_{ia} and Q_{bf} are equal to zero since they are adiabatic processes resulting in $\left(W_{if} \right) = \left(W_{iabf} \right) = \left(W_{ia} + W_{ab} + W_{bf} \right)$. Therefore, the result becomes $\left[Q_{ab} - W_{if} = \left(U_f - U_i \right) \right]$ giving the final result that $\left(Q_{ab} = Q_{if} \right)$. In general, therefore, an arbitrary reversible process can always be replaced by a zigzag path between the same state points consisting of a reversible adiabatic line, a reversible isotherm, and another reversible adiabatic line, such that $\left\{ Q_{originalprocess} = Q_{isotherm} \right\}$.
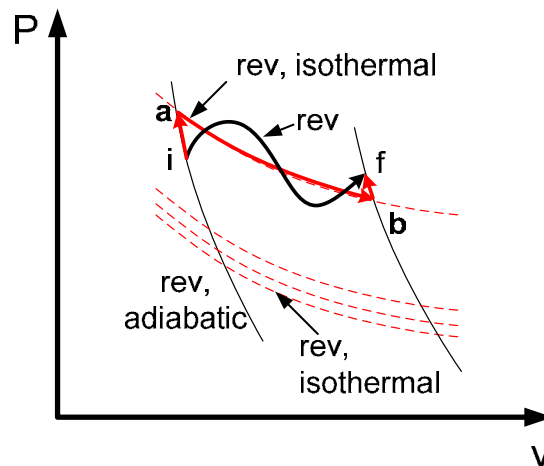
Fig 3. Development of the Carnot cycle.

Now the heat terms give $\left(Q_{if} = Q_{iabf}\right)$ since (U_f − U_i) does not change because of the general character of a thermodynamic property. Also Q_{ia} and Q_{bf} are equal to zero since they are adiabatic processes resulting in $\left(W_{if}\right) = \left(W_{iabf}\right) = \left(W_{ia} + W_{ab} + W_{bf}\right)$. Therefore, the result becomes $\left[Q_{ab} - W_{if} = \left(U_f - U_i\right)\right]$ giving the final result that $\left(Q_{ab} = Q_{if}\right)$.   In general, therefore, an arbitrary reversible process can always be replaced by a zigzag path between the same state points consisting of a reversible adiabatic line, a reversible isotherm, and another reversible adiabatic line, such that $\left\{Q_{originalprocess} = Q_{isotherm}\right\}$.
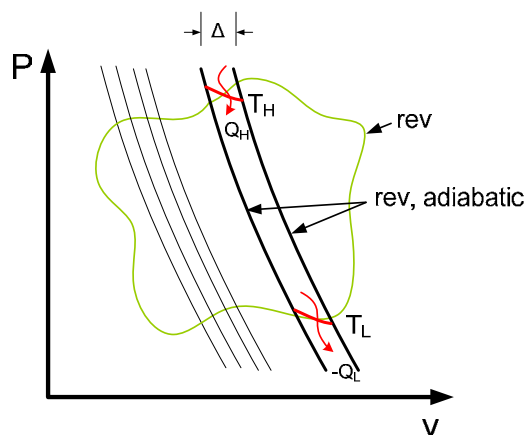

Fig 4. Development of Clausius' statement and entropy.

Now, to reach the definition of thermodynamic quantity entropy, consider a smooth reversible cycle as shown in Fig. 4. On it inscribe reversible adiabatic lines of thickness Δ. For each slice or arc, which is a reversible process, inscribe an isotherm so that the

condition given above is satisfied. The cycles thus formed are all Carnot cycles with the characteristic relationship obtained between heat transfer and absolute temperature ratios. Thus for the first cycle drawn, $\left\{ \dfrac{Q_{H_1}}{-Q_{L_1}} = \dfrac{T_{H_1}}{T_{L_1}} \right\}$ or $\left\{ \dfrac{Q_{H_1}}{T_{H_1}} + \dfrac{Q_{L_1}}{T_{L_1}} = 0 \right\}$.

In a similar fashion, for the second cycle we have $\left\{ \dfrac{Q_{H_2}}{T_{H_2}} + \dfrac{Q_{L_2}}{T_{L_2}} = 0 \right\}$.

Adding these two results and generalizing for the sum of all such cycles, then $\left\{ \sum_i \dfrac{Q_i}{T_i} = 0 \right\}$.

In the limit as $\Delta \to 0$, the adiabatic lines come closer thus making the heat quantities infinitesimal resulting in $\left\{ \oint_{rev} \dfrac{\delta Q}{T} = 0 \right\}$ which is the important Clausius theorem.
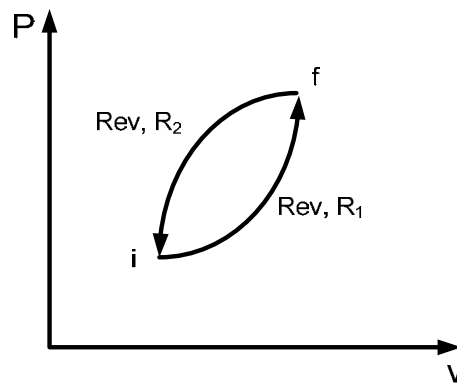

Fig. 5. A reversible cycle.

Now consider two reversible processes R_1 and R_2 starting from the initial state i and ending at the final state f, Fig. 5. Since they are reversible, it is possible to change the sense of R_2. Since R_1 and R_2 now form a reversible cycle, then $\left\{ \oint_{R_1 R_2} \dfrac{\delta Q}{T} = 0 \right\}$ and $\left\{ \int_{i_{R_1}}^{f} \dfrac{\delta Q}{T} + \int_{f_{R_2}}^{i} \dfrac{\delta Q}{T} = 0 \right\}$. This results in the most general relation for the integral in a reversible process $\left\{ \int_{i_{R_1}}^{f} \dfrac{\delta Q}{T} \right\} = \left\{ \int_{i_{R_2}}^{f} \dfrac{\delta Q}{T} \right\} = \ldots = \left\{ \int_{i_R}^{f} \dfrac{\delta Q}{T} \right\}$ which says that if a reversible path is chosen, the path itself is not important so long as the process starts at i and ends at f. The quantity is, therefore, given by the end states and not the path. As is the case in the first law of thermodynamics, $\left[\oint \delta Q - \oint \delta W = \oint dU \right]$ and $\left(\oint dU = 0 \right)$ since internal energy is

a thermodynamic property, then $\left\{ \oint_{rev} \dfrac{\delta Q}{T} = 0 \right\}$ is a thermodynamic property and is called

entropy, S. Therefore, $\left\{ \int_{i_{REV}}^{f} dS = \left(S_f - S_i\right) \right\}$ or for an infinitesimal process, $\left\{ \dfrac{\delta Q_{rev}}{T} = dS \right\}$

that forms the mathematical formulation of the second law of thermodynamics. It is, therefore, seen that there is a similarity between the two laws of thermodynamics and their definition of internal energy and entropy. To further extend this discussion to the inequality of Clausius, consider the fact that all heat engines operating between a given high temperature source, T_H, and a lower temperature sink of T_L, none can have a higher efficiency than the Carnot engine. Thus using the figure above, but this time having the process at T_H to be irreversible, then the result obtained is

$$\left(1 + \frac{Q_{L_{REV}}}{Q_{H_{IRREV}}} \right) \le \left(1 + \frac{Q_L}{Q_H} \right)_{REV} .$$

Using the fact that $\left\{ \dfrac{-Q_L}{Q_H} = \dfrac{T_L}{T_H} \right\}$ is for reversible energy transfers, then

$$\left(\frac{Q_{L_{REV}}}{Q_{H_{IRREV}}} \right) \le \left(1 - \frac{T_L}{T_H} \right).$$

Transposing and keeping in mind that there is a negative sign, the result becomes

$$\left(\frac{\delta Q_{L_{REV}}}{T_L} \right) \ge \left(\frac{\delta Q_{H_{IRREV}}}{T_H} \right).$$

Using the definition of entropy as given above, $dS \ge \left(\dfrac{\delta Q_{H_{IRREV}}}{T_H} \right)$ or $\oint dS \ge \left(\dfrac{\delta Q}{T} \right)_{IRREV}$

which states that in all real processes entropy increases and the equality is only for the reversible process. This further reduces the result to what is expected, the inequality of Clausius, the fact that $\oint \left(\dfrac{\delta Q}{T} \right)_{IRREV} \le 0$.

If the entropy changes of the system are added to the entropy changes occurring in the surroundings as a result of the changes in the system, the sum represents the total changes of the system and the surroundings and is called the entropy change of the universe or entropy generation, σ. For a reversible process, let δQ$_{rev}$ amount of energy be absorbed by the system.

Then $\left(dS_{system} = \dfrac{\delta Q_{rev}}{T} \right) > 0$ since it has been put into the system. Since this energy has

to be given up by the surroundings, then $\left(dS_{surroundings} = \dfrac{\delta Q_{rev}}{T} \right) < 0.$

As a result, the entropy generation is $\left(dS_{universe} = d\sigma = 0\right)$. Thus, when a reversible process is performed, the entropy of the universe remains unchanged.

The second law representation of the systems that we are interested in is as follows:

Closed system:
$$\Delta\sigma = m(s_2 - s_1) - \sum_j (\frac{Q_j}{T_j})_{12}$$

Open system:
$$\Delta\dot{\sigma} = \sum_e (\dot{m}s) - \sum_i (\dot{m}s) - \sum_j (\frac{\dot{Q}_j}{T_j})_{ie}$$

Filling system:
$$\Delta\sigma = m_2 s_2 - \sum_i (ms) - m_1 s_1 - \sum_j (\frac{Q_j}{T_j})_{ie}$$

Emptying system:
$$\Delta\sigma = \sum_e (ms) + m_2 s_2 - m_1 s_1 - \sum_j (\frac{Q_j}{T_j})_{ie}$$

The product of the environment temperature T_0 with $\Delta\sigma$ is called the irreversibility, I_{ie} of the process. Therefore, either entropy generation or irreversibility can be used to discuss the given situation. It is not important which choice is made. It is this irreversibility that gives rise to pollution and degradation of the environment leading to unsustainability of the present quality of life in nature.

9. Exergy

Exergy or available energy is the capacity to perform useful work with a given amount of energy. This can also be considered as the taxation of energy by nature. What nature is saying that although we may have an amount of energy that we should be able to use, the portion of that energy between the lowest available temperature T_0[K] and 0[K] is the amount that is taken out by nature before any useful work can be obtained, $(T_0\Delta S)$. Unlike the government's share of our income as taxes, this amount is not negotiable. Therefore, this amount goes back to nature, unfortunately in the form of pollution. This result also states that if we want to produce useful products, such as electricity or transportation, we agree to pollute the environment. Thus to be conscious of our responsibilities to our and future generations, better conversion technologies and conservation seem to be the only immediate solutions since any power generation MUST produce pollution of some sort that we may not be able to accept. Intelligent use of resources, therefore, must happen; otherwise the consequences are not very desirable.

The exergy formulation for the systems that we are interested in are given below without a detailed derivation. However, the principles presented above suffice to obtain them.

Closed system:

$$A_{12} = \sum_j Q_j (1 - \frac{T_0}{T_j}) + (U_1 - U_2) + p_0(V_1 - V_2) - T_0(S_1 - S_2) - T_0 \Delta \sigma$$

Open system:

$$\dot{A}_{ie} = \sum_j \dot{Q}_j (1 - \frac{T_0}{T_j}) + \sum_i \dot{m}[(h - T_0 s) + \frac{\bar{V}^2}{2} + gz] - \sum_e \dot{m}[(h - T_0 s) + \frac{\bar{V}^2}{2} + gz] - T_0 \Delta \sigma$$

Filling system:

$$A_{ie} = \sum_j Q_j (1 - \frac{T_0}{T_j}) + \sum_i m[(h - T_0 s) + \frac{\bar{V}^2}{2} + gz] + m_1(u_1 + p_0 v_1 - T_0 s_1) - m_2(u_2 + p_0 v_2 - T_0 s_2) - T_0 \Delta \sigma$$

Emptying system:

$$A_{ie} = \sum_j Q_j (1 - \frac{T_0}{T_j}) - \sum_e m[(h - T_0 s) + \frac{\bar{V}^2}{2} + gz] + m_1(u_1 + p_0 v_1 - T_0 s_1) - m_2(u_2 + p_0 v_2 - T_0 s_2) - T_0 \Delta \sigma$$

Use of these equations will give us the availability of energy, or exergy, for maximum obtainable work in any given system.

10. Nonmeasurable thermodynamic properties

The classical method of eliminating non-measurable thermodynamic properties is successive use of the Maxwell relations. However, this method is very time consuming at times since one does not know exactly in which direction the elimination must take place. Sometimes, due to this uncertainty, it does not work There is a method, however, called the method of Jacobians which accomplish the same result in a very systematic way without any guess work, Somerton and Arnas (1985). Although the method was first introduced fifty years prior to this, the only text known that discuss these is that of Callen (1960).

This methodology has been used extensively to explain certain thermodynamic phenomena, to design experiments, and to eliminate the non-measurable thermodynamic properties, Arnas (2000). The measurable thermodynamic properties are p, T, V. Also the specific heats at constant pressure and volume, respectively, $c_p = T\left(\frac{\partial s}{\partial T}\right)_p$ and $c_v = T\left(\frac{\partial s}{\partial T}\right)_v$, the coefficient of thermal expansion, $\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$, and the isothermal compressibility, $\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$ of substances can be measured.

Using these parameters and since thermodynamic properties are mathematically well behaved functions, namely the order of differentiation does not make any difference, i.e.

$$\left[\frac{\partial}{\partial X}\left(\frac{\partial Z}{\partial Y}\right)\right] = \left[\frac{\partial}{\partial Y}\left(\frac{\partial Z}{\partial X}\right)\right]$$ the elimination of the non-measurable properties becomes simple.

In general, the Maxwell relations are obtained from {dZ=M dX + N dY} as $\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y$. Since U = U(S,V) then $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S$. Comparing this equation to the Gibbs' equation, {dU=T dS − p dV}, it is seen that $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -p$.

Additionally, using the above property, we can get the equality $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$.

Similar equalities can be obtained using the other Gibbs equations that relate other properties, i.e. enthalpy, H = H (S, p) and {dH = T dS + V dp}, the Gibbs function G = G(T,p) and {dG = - S dT + V dp}, and the Helmholtz potential F = F(T,V) and {dF = -S dT − p dV}. These are also useful in elimination of some of the non-measurable terms and thermodynamic properties.

In Somerton and Arnas (1985), the theory as well as the use of the method is given. For the general equation of {dZ = M dY + N dX}, the Jacobian formulation can be written as {[Z,ξ] = M[Y,ξ] + N[X,ξ]} where ξ is any other thermodynamic property. Also, the equalities [Z,Z] ≡ 0, [Z,ξ]=-[ξ,Z], and $\left(\frac{\partial(X,Y)}{\partial(X,Y)}\right) = 1$ are very useful.

From fundamentals of mathematics we have $\frac{\partial Y}{\partial X} = \left(\frac{\partial Y}{\partial \xi}\right)\left(\frac{\partial \xi}{\partial X}\right)$.

Using the first law of thermodynamics for a cycle, we get $\left(\oint \delta Q = \oint \delta W\right)$ since $\left(\oint dU\right) = 0$.

In Gibbs form, {dU=TdS − pdV} giving for a cycle [T ds = p dV] which in Jacobian form becomes [T,S] = [p,V]. The systematic use of these will permit one to convert nonmeasurable terms into measurable ones including p, V, T, c_p, c_v, α, and κ_T.

The general methodology, therefore, is:

1. Write down the given in terms of Jacobians.

2. Reduce by Maxwell equations using the various Gibbs equations.

3. Use the definition of c_p, c_v, α, and κ_T to further reduce the given equation.

4. If everything is done correctly, the result should only contain p, v, T, c_p, c_v, α, and κ_T. If not, an error has been made; you need to go back and redo everything.

If this methodology is not used, then one goes around and around until a solution is obtained and one does not know if the route taken is the correct one. The advantage of the method of Jacobians is that the result shows if a mistake has been made.

The examples given in Somerton and Arnas (1985) are for learning the methodology. We will also look at other relations and get the physical significance of some other important thermodynamic phenomena, for example throttling,

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h = \left\{\frac{1}{c_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]\right\}$$

and the speed of sound in any medium,

$$c^2 = \left(\frac{\partial p}{\partial \rho}\right)_s = \left[\frac{\partial p}{\partial\left(\frac{1}{v}\right)}\right]_s = \left\{-\left(\frac{c_p}{c_v}\right)v^2\left(\frac{\partial p}{\partial v}\right)_T\right\}.$$

As an example, start with $c_v = T\left(\frac{\partial s}{\partial T}\right)_v$.

Therefore, following the methodology given,

STEP 1: $\left(\frac{\partial s}{\partial T}\right)_v \equiv \frac{\partial(s,v)}{\partial(T,v)}\left(\frac{\partial(p,T)}{\partial(p,T)}\right) = -\left[\frac{\partial(s,v)}{\partial(p,T)}\right]\bigg/\left[\frac{\partial(v,T)}{\partial(p,T)}\right]$

STEP 2: However, the denominator is by definition {-v κ$_T$}. Therefore,

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{v\kappa_T}\left[\frac{\partial(s,v)}{\partial(p,T)}\right] = \frac{1}{v\kappa_T}\begin{vmatrix}\left(\frac{\partial s}{\partial p}\right)_T & \left(\frac{\partial s}{\partial T}\right)_p \\ \left(\frac{\partial v}{\partial p}\right)_T & \left(\frac{\partial v}{\partial T}\right)_p\end{vmatrix}$$

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{v\kappa_T}\left[\left(\frac{\partial s}{\partial p}\right)_T\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial s}{\partial T}\right)_p\left(\frac{\partial v}{\partial p}\right)_T\right]$$

Using the Maxwell relation, $\left(\dfrac{\partial s}{\partial p}\right)_T = -\left(\dfrac{\partial v}{\partial T}\right)_p$ which comes from the Gibbs form of the

Gibbs' function equation, and the definitions of c_p, α, and κ_T,

$$\frac{c_v}{T} = \frac{1}{v\kappa_T}\left[-(\alpha^2 v^2 + \frac{c_p}{T}(v\kappa_T)\right].$$

Rearranging, $\left[(c_p - c_v) = Tv\dfrac{\alpha^2}{\kappa_T}\right].$

For an ideal gas, this general result reduces to $(c_p - c_v) = \dfrac{\Re}{M}$, where $\Re$ is the Universal

gas constant and M is the molecular mass of the ideal gas, a well known relationship. It is also possible to show that for an incompressible substance, i.e. liquid water, $(c_p - c_v) = 0$ which says that for those we must just use $\underline{c}$ as the specific heat without any subscripts. For those substances for which we have tables, enthalpies must be used and not $\Delta h = c\Delta T$, another common mistake in literature, Çengel and Boles (2008). In analyzing other derivatives of interest, these methodologies become very useful as well when we go

through those quantities, for example $\left(\dfrac{\partial U}{\partial V}\right)_T$ and $\left(\dfrac{\partial H}{\partial p}\right)_T$, and their values for an ideal

gas. In Arnas (2000), these along with other characteristics are further studied. The slope

of various functions on the Mollier chart, an (h-s) diagram, i.e. $\left(\dfrac{\partial h}{\partial s}\right)_T = \left\{T - v\left(\dfrac{\partial T}{\partial v}\right)_p\right\}$,

$\left(\dfrac{\partial h}{\partial s}\right)_p$, $\left(\dfrac{\partial h}{\partial s}\right)_v$, and other thermodynamic diagrams, such as the (p-h) for refrigerants,

i.e. $\left(\dfrac{\partial p}{\partial h}\right)_s = \left\{-\dfrac{\left(\dfrac{c_p}{c_v}\right)}{p}\left(\dfrac{\partial p}{\partial v}\right)_T\right\}$, is also explained to clarify the physics involved; for an

ideal gas, this reduces to $\left(\dfrac{\partial p}{\partial h}\right)_s = \dfrac{\left(\dfrac{c_p}{c_v}\right)}{v} = \dfrac{k}{v}$, where k is the ratio of the specific heats,

$\left(k = \dfrac{c_p}{c_v}\right).$

To obtain pressure-temperature relation for an ideal gas under reversible adiabatic

conditions, we start with $\left(\dfrac{\partial p}{\partial T}\right)_s = \left[\dfrac{p,s}{T,s}\right] = -\left[\dfrac{s,p}{T,s}\right].$ Substituting for the numerator and

the denominator from Jacobian properties, then we get

$$\left(\frac{\partial p}{\partial T}\right)_s = \frac{-\dfrac{c_p}{T}[T,p]}{[p,v]} = \frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_p \quad \text{which is a general result.}$$

Using the ideal gas equation, the partial derivative on the right can be evaluated. Using the difference between the two specific heats for an ideal gas, as was shown above, the result becomes $\left(\dfrac{\partial p}{\partial T}\right)_s = \dfrac{p c_p}{T\left(\dfrac{\Re}{M}\right)} = \dfrac{p}{T}\left(\dfrac{k}{k-1}\right).$

Therefore, $\left(\dfrac{dp/p}{dT/T}\right) = \dfrac{k}{k-1}$ which, upon integration gives the well known result

$$\left[T = p^{\frac{k-1}{k}}\right].$$

This result is only valid if we have an ideal gas which undergoes a reversible and adiabatic, constant entropy, process. Again, this fact is not trivial and must be kept in mind before this result can be used. Similar results can be obtained for $\left(\dfrac{\partial v}{\partial T}\right)_s = -\dfrac{c_v}{T}\left(\dfrac{\partial T}{\partial p}\right)_v$, in general, and applied to an ideal gas would give, $\left(\dfrac{dv/v}{dT/T}\right) = -\left(\dfrac{1}{k-1}\right)$or $\left[T = v^{1-k}\right].$ For $\left(\dfrac{\partial p}{\partial v}\right)_s$ we get the result, in general, $\left(\dfrac{\partial p}{\partial v}\right)_s = k\left(\dfrac{\partial p}{\partial v}\right)_T.$

This equals for an ideal gas $\left(\dfrac{dp/p}{dv/v}\right) = -k$ giving $\left[p = v^{-k}\right].$

The total intent in all this was to verify the physics of the situation using mathematics. Mathematics is just a tool to totally explain these physical phenomena that characterize nature. Nature is what physics is; mathematics is the explanation mechanism and nothing more.

11. Design of Experiments

In engineering, experimental verification of analysis or computational results is extremely important. For that, it is necessary to design experiments. Experiments can only be designed for those parameters for which we can make measurements. As was discussed before, the measurable parameters in thermodynamics are p, T, V, c_p, c_v, α, and κ_T. Therefore, the designed experiment can only involve these parameters.

As an example of this important issue, consider the Clausius' equation which is

$$\left(\frac{dp}{dT}\right)_{saturation} = \left\{\frac{Q_{12}}{T(v_2 - v_1)}\right\}.$$

By considering the T-s diagram, it is obvious that the heat transferred is equal to $Q_{12} = T(s_2 - s_1)$. From the Gibbs' equation for enthalpy, {dh = T ds + v dp}, and since at saturation the pressure and temperature are constants, then {dh = T ds} giving $[(h_2 - h_1) = T(s_2 - s_1)]$.

Upon substitution, $\left(\frac{dp}{dT}\right)_{saturation} = \left\{\frac{(h_2 - h_1)}{T(v_2 - v_1)}\right\}$, where 2 refers to the saturated vapor

state, g, and 1 to the saturated liquid state, f.

Therefore, the Clausius equation becomes, $\left(\frac{dp}{dT}\right)_{saturation} = \frac{h_{fg}}{Tv_{fg}}$.

Clapeyron modified this equation by making certain assumptions. The first assumption is that $v_g \gg v_f$ which is an acceptable one since the vapor specific volume is much greater numerically than the liquid specific volume, as can be seen in the Steam Tables, Çengel and Boles (2008). The second assumption is that of an ideal gas for the vapor, i.e. $v_g \cong v = \left(\frac{\Re}{M}\right)\left(\frac{T}{p}\right)$ which, upon substitution, makes the Clausius' equation

$$\left(\frac{dp}{dT}\right)_{saturation} = \left(\frac{h_{fg}}{\left[\frac{\Re}{M}\right]}\right)\left(\frac{p}{T^2}\right).$$

Collecting like terms, this equation reduces to $\left[\frac{\left(\frac{dp}{p}\right)}{\left(\frac{dT}{T^2}\right)}\right] = \left(\frac{h_{fg}}{\left[\frac{\Re}{M}\right]}\right).$

Considering that h_{fg} is a constant, an assumption that needs to be verified for the design of the experiment, and integrating and simplifying, the Clausius-Clapeyron equation is obtained as

$$\left[\frac{d(\ln p)}{d\left(\frac{1}{T}\right)}\right] = -\left(\frac{h_{fg}}{\left[\frac{\Re}{M}\right]}\right)$$ which is only valid <u>if</u> $v_g \gg v_f$ <u>and</u> we have an ideal gas for constant

h_{fg}.

All of these three assumptions must be satisfied before the results of the experiment can have any significance. Therefore in the design of the experiment we must consider these facts very carefully.

In designing an experiment, the first assumption for the Clausius-Clapeyron equation is satisfied when one looks in the Steam Tables, Çengel and Boles (2008), to compare the numerical values of the specific volume as a vapor and a liquid. The second assumption, an ideal gas, requires some more discussion. When we look at the compressibility diagram for substances, we see that the compressibility for all substances approach unity, meaning they approach the characteristics of an ideal gas, as the reduced pressure of the substance approaches zero, i.e $Z \Rightarrow 1$ as $p_{\text{Reduced}} = \dfrac{p}{p_{critical}} \Rightarrow 0.$ This result signifies that the experiment must take place at low real pressures, i.e. below atmospheric, since the critical pressure for steam is 22.09[MPa] to make sure that we are approaching zero for the reduced pressure to guarantee ideal gas situation. Finally, constant h_{fg} assumption requires that the measurements must take place at a pressure an increment above and an increment below the saturation pressure under investigation. By taking this increment small and splitting it up for as many precise measurements as possible, all that is needed to do is to plot (ln p) versus $\left(\dfrac{1}{T}\right)$ using the absolute temperature. The slope of the line is negative, as the Clausius-Clapeyron equation requires, and will give the value h_{fg} once the molecular mass of water is used. Other fluids can also be used in this experiment; the only requirement is to make sure that $Z \Rightarrow 1$ and $p_{\text{Reduced}} = \dfrac{p}{p_{critical}} \Rightarrow 0$ for the liquid that is used.

For the speed of sound or the Joule-Thomson coefficient similar experiments can be designed, constructed, and experimental results can be obtained once their measurable forms are derived, as was done above. This methodology is good for any quantity for which an experiment is to be designed; the important thing to keep in mind is the assumptions under which the result is obtained. If any one of the assumptions is not met, then the experiment will not give the expected results.

This, of course, is not different from any scientific/engineering analysis or experiment. The results obtained are only as good as the assumptions made and that the results are only valid under those assumptions. This may sound trivial but we will show that it is a mistake made quiet commonly by researchers and/or authors of textbooks.

12. Errors made in literature

When one studies the literature carefully, one does find fundamental errors made due to the fact that simple understanding of thermodynamics is lacking. As we have already discussed very early on the state principle and the fact that any two independent intensive

thermodynamic properties are sufficient to define a thermodynamic state, it is really of no consequence which two are selected since the final result has to be unique.

Chawla (1978) selects three different combinations of properties to determine the speed of sound. In the first case, the variables selected are the velocity, the pressure, and the enthalpy. The result for the speed of sound turns out to be

$$c^2 = \frac{1}{\left(\dfrac{\partial \rho}{\partial p}\right)_h + \dfrac{1}{\rho}\left(\dfrac{\partial \rho}{\partial h}\right)_p}$$

where ρ is the density, inverse of v. The second case is for the velocity, the density, and the pressure. This time the result obtained becomes

$$c^2 = \left[\frac{-\rho\left(\dfrac{\partial h}{\partial \rho}\right)_p}{\rho\left(\dfrac{\partial h}{\partial p}\right)_\rho - 1}\right].$$

The third case is for the velocity, the pressure and the temperature. The result obtained is,

$$c^2 = \frac{1}{\left\{\left[\dfrac{\left[-\left(\dfrac{\partial \rho}{\partial T}\right)_p\right]}{\rho c_p}\right]\left[\rho\left(\dfrac{\partial h}{\partial p}\right)_T - 1\right] + \left(\dfrac{\partial \rho}{\partial p}\right)_T\right\}}.$$

However, from the definition of the speed of sound, $c^2 = \left(\dfrac{\partial p}{\partial \rho}\right)_s$ and using the methodology given above, it is indeed very simple to show that the analytical result is

$$c^2 = -v^2\left(\frac{\partial p}{\partial v}\right)_s = -v^2\left[\frac{p,s}{v,s}\right] = -v^2\left(\frac{c_p}{c_v}\right)\left(\frac{\partial p}{\partial v}\right)_T.$$

No matter which two properties along with the velocity is chosen, this is the result that must be obtained. Results are obtained in terms of nonmeasurable properties which are consequently solved numerically, Chawla (1978). Since the series variation of these properties do not have the same character, numerical truncation errors result in different forms for the answers. The author then tries to justify why they are different. However, we have seen that the result has got to be unique, the state principle, and it is demonstrated once again by Arnas (2000). All three results above analytically are the same, as it should be. Numerically, they are not! Therefore, a fundamental understanding of thermodynamics is very important to explain physical phenomena.

13. Shortcomings of textbooks

Apart from the shortcomings of books on Thermodynamics, and there are many, similar shortcomings that exist in other textbooks because of lack of being precise that discuss, for example, Heat Transfer which is an applied course heavily dependent on thermodynamic principles. The student is learning from the textbooks; therefore, they trust the contents as they must. However, if the topics are not precisely covered, then they learn the wrong material.

As an example, we will consider condensation phenomena since it is an important process in thermodynamics, as we have discussed above in the case of the Clausius-Clapeyron equation and the steam experiment, and since we must design condensers for technological purposes, using heat transfer. When one considers the condensation phenomenon as discussed in textbooks, also as was done by Arnas et. al (2004), there are many assumptions that are made to be able to analyze the physical situation. Unfortunately in all of these, the assumptions that are made are not justified for the final result. The final result is the same in all of the references, the only thing different are the symbols used. However, the student does not know if a given situation actually satisfies all the assumptions made. Therefore, for all situations, the only design equation is the one found in the texts and that one is used blindly. It is indeed possible to find situations where anyone of these conditions is not met which would make the equation useless. In Arnas et.al (2004) not only is the result obtained very rigorously and in a very clear and analytical fashion, the conditions under which the result is valid are also very clearly given so that the user, the student, researcher or the design engineer is able to ascertain if the problem actually fits the final design equation for convection in condensation.

In another study by Arnas et. al (1980), it was shown that the two-phase flow design equations are not usable under all conditions since they tend to decrease the entropy generation for certain combinations of flow rates and geometries; a condition that violates the second law of thermodynamics. Naturally, under those conditions the equations cannot be used for design purposes and other correlations must be searched.

What has been attempted here is to show the importance of correct use of precise thermodynamics in teaching of thermodynamics as well as in all other fields of science and technology. If it is not used precisely, errors are made that could affect the designed equipment or lead to disastrous situations in extreme cases. In engineering we cannot make mistakes since, unlike the doctor, we do not kill one person at a time! Our failures are watched and seen by the whole world, for example the Space Shuttle disaster. We must teach well, in a correct way, and precisely and demand of our students at all levels the same precision in their work, Arnas (2005). Only in that fashion can be sure that the next generation of engineers/scientists understands the critical ramifications of what is at stake. This is more important than anything else that we can teach our students; their understanding and appreciation of the importance of their precise work.

14. Conclusions

In this paper, the precise teaching of thermodynamics has been emphasized since these topics are used in other fields of science and technology. The textbooks must be correct giving the precise description of systems, equations and conclusions. Otherwise the students learn the wrong information and apply it in the same fashion. It has also been shown that methodologies exist for physical interpretation of mathematical expressions in thermodynamics by eliminating nonmeasurable quantities such as entropy, designing thermodynamic experiments and investigating various applications in other fields of science and technology that use thermodynamic principles. The emphasis has been in correct and precise work, a quality that we must impose on our students. This type of instruction would ultimately affect students who are aware of the nature, the effect of everyday usage of energy on the environment, and what needs to be done within the restrictions of nature to be sustainable at least at the levels that we enjoy today. Of course, these must be done in all aspects of education not only in the education of engineers, in general, and thermodynamics education, in particular. Success in this will make life better now and forever.

The previous pages have emphasized undergraduate work. It is indeed very important to extend this into statistical and nonequilibrium thermodynamics for graduate students. The challenges of energy use, pollution and sustainability all depend on clear, precise and correct study of these and appropriate applications. It can and should be pursued very aggressively throughout.

Acknowledgement

The view expressed herein are those of the author and do not purport to reflect the position of the Unites States Military Academy, the Department of the Army, or the Department of Defense.

Nomenclature

A   Area [m^2]

B   Any extensive thermodynamic property

b   Any intensive thermodynamic property, b=B/m

c   Specific heat [kJ/(kg-K)]; also speed of sound [m/s]

E   Energy [kJ]

e   specific energy [kJ/kg]

F   Helmholtz potential [kJ]

G   Gibbs free energy [kJ]

H	Enthalpy [kJ]
h	Specific enthalpy [kJ/kg]
k	Ratio of specific heats, $k=(c_p/c_v)$
M	Molecular mass [kmol]; also arbitrary function
m	Mass [kg]
$\dot{m}$	Mass flow rate [kg/s]
N	Arbitrary function
n	Unit vector
p	Pressure [kPa]
Q	Heat [kJ]
$\Re$	Universal gas constant [kJ/(kmol-K)]
S	Entropy [kJ/K]
s	Specific entropy [kJ/(kg-K)]
T	Temperature [K]
t	Time [s]
U	Internal energy [kJ]
u	Specific internal energy [kJ/kg[
V	Volume [m^3]
v	Specific volume [m^3/kg]
$\vec{V}$	Velocity [m/s]
W	Work [kJ]
X	Arbitrary function
Y	Arbitrary function
Z	Arbitrary function; also compressibility factor [-]
z	Elevation [m]

Greek symbols

α	Coefficient of thermal expansion [1/K]
β	Coefficient of performance for a refrigerator
γ	Coefficient of performance for a heat pump
Δ	Difference
δ	Increment

η   Efficiency for an engine

Θ   Angle [^{o}]

κ$_T$ Isothermal compressibility [1/kPa]

μ   Joule-Thomson coefficient [K/kPa]

ξ   Arbitrary thermodynamics property

ρ   Density [kg/m^3]

σ   Entropy generation [kJ/K]

Subscripts

E   Engine

CE   Carnot engine

CV   Control volume

f   Liquid phase

fg   Phase change from liquid to vapor

g   Vapor phase

H   High

L   Low

v   Volume

p   Pressure

o   Atmospheric

References

[1]. Arnas AÖ (2000) *On the Physical Interpretation of the Mathematics of Thermodynamics.* **International Journal of Thermal Sciences 39**: 551-555

[2]. Arnas AÖ (2005) *Education, Energy, Exergy, Environment – Teaching Teachers to Teach Thermodynamics*, **Proceedings**, Second International Exergy, Energy and Environment Sysmposium-IEEES2, Kos, Greece, #167.

[3]. Arnas AÖ, Hendrikson HAM, van Koppen CWJ (1980) *Thermodynamic Explanation of Some Numerical Difficulties in Multiphase Flow Analyses*, **Proceedings**, European Two-Phase Flow Group Meeting, Glasgow, Scotland, F4.

[4]. Arnas AÖ, Boettner DD, Bailey MB (2003) *On the Sign Convention in Thermodynamics-An Asset or an Evil*, **Proceedings**, ASME-IMECE2003, IMECE2003-41048. Also, Boettner DD, Bailey MB, Arnas AÖ (2006) *On the Consistent Use of Sign Convention in Thermodynamics*, **International Journal of Mechanical Engineering Education 34**/4: 330-348

[5]. Arnas AÖ, Boettner DD, Benson MJ, van Poppel BP (2004) *On the Teaching of Condensation Heat Transfer*, **Proceedings**, ASME-IMECE2004, IMECE2004-50277. Also, Tamm G, Boettner DD, van Poppel BP, Benson MJ, Arnas AÖ (2009) *On the Similarity Solution for Condensation Heat Transfer*, **ASME Journal of Heat Transfer 131:** 111501-1/5

[6]. Callen HB (1960) **Thermodynamics**, Wiley.

[7]. Çengel YA, Boles ME (2008) **Thermodynamics-An Engineering Approach**, 6th Edition, McGraw-Hill.

[8]. Chawla TC (1978) *On Equivalency of the Various Expressions for Speed of Wave Propagation for Compressible Liquid Flows with Heat Transfer*, **International Journal of Heat and Mass Transfer 21**: 1431-1435.

[9]. Mooney DA (1953) **Mechanical Engineering Thermodynamics**, Prentice-Hall.

[10]. Obert EF (1960) **Concepts of Thermodynamics**, Wiley.

[11]. Somerton CW, Arnas AÖ (1985) *On the Use of Jacobians to Reduce Thermodynamic Derivatives*, **International Journal of Mechanical Engineering Education 13**-1: 9-18.

[12]. Zemansky MW (1943) **Heat and Thermodynamics**, Wiley.

EXERGY-BASED METHODS APPLIED TO THE CHAIN "NATURAL GAS – LNG – NATURAL GAS"

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Abstract

The liquefied natural gas (LNG) market was established in the 1960s. During its over 50 years history, this market has grown significantly and the growth is expected to continue in the future. New technologies that lead to an increased efficiency in each step of the LNG chain are permanently in the focus of consideration. The overall chain "natural gas − LNG – natural gas" can be divided into four blocks: (a) Export terminal with associated technology for natural gas liquefaction (LNG production), (b) LNG transport, (c) import terminal using a regasification process, and (d) distribution of the natural gas. Each of those four blocks is associated with energy-intensive processes.

The paper discusses the application of exergy-based methods to these processes.

Keywords: *LNG; Exergy-Based Methods; Advanced Exergy-Based Methods*

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List of Symbols

$\dot{B}$	: environmental impact rate associated with an exergy stream (Points)	**Greeks**	
		ε	: exergetic efficiency (%)
b	: environmental impact *per unit of exergy* (Points/J) or per unit of mass (Points /kg)	η	: isentropic efficiency of a pump/compressor (%)
$\dot{C}$	: cost rate associated with an exergy stream (US$/s)	**Subscripts**	
		b	refers to environmental impact
c	: cost per unit of exergy (US$/J) or per unit of mass (US$/kg)	D	exergy destruction
		F	exergy of fuel
$\dot{E}$	: exergy rate (MW)	k	k^{th} component
e	: specific exergy (MJ/kg)	L	exergy loss
f	: exergoeconomic factor (-)	P	exergy of product
k	: k^{th} component or k^{th} substance	tot	overall system
$\dot{m}$	: mass flow rate (kg/s)	w	power (electricity)
p	: pressure (bar)	0	thermodynamic
$\dot{Q}$	: heat rate (W)		environment
r	: relative cost difference (%)		(reference state)
T	: temperature (ºC)	**Subscripts**	
$\dot{W}$	: power (MW)	AV	avoidable
y	: exergy destruction ratio (%)	CH	chemical
Y	: cost of component-related environmental impact (Points/h)	M	mechanical
		PH	physical
$\dot{Z}$	: cost rate associated with investment expenditures (US$/h)	T	thermal
		UN	unavoidable

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1. Introduction

The overall chain "natural gas − LNG – natural gas" can be divided into four blocks:

a) Export terminal with associated technology for liquefaction of natural gas (LNG production),

b) LNG transport,

c) Import terminal using a regasification process, and

d) Distribution of natural gas.

Based on data that were available at the end of the year 2010, worldwide there are

- 25 LNG liquefaction plants (with multi-train arrangement), and
- 83 LNG regasification plants (including 10 floating structures).

The price of LNG, obviously, depends on the price of natural gas. However, the price of LNG is also affected by the cost of the liquefaction, shipping and regasification processes.

The total capital investment associated with the LNG chain can be divided as follows: Exploration – between 15% and 20%; liquefaction and storage – between 30% and 45%; shipping – between 10% and 30%; and storage and regasification – between 15% and 25%.

The following liquefaction processes were in use at liquefaction plants (with the corresponding liquefaction capacity for each type of technology) in the year 2010:

- C_3MR (by Air Products and Chemicals) – 55%
- C_3MR/Split MR (by Air Products and Chemicals) – 12%
- AP-X (by Air Products and Chemicals) – 12%
- Optimized Cascade (by ConocoPhillips) – 12%
- Dual Mixed Refrigerant (by Shell) – 4%
- Mixed Fluid Cascade (by Linde) – 2%
- Others – 3%

Each of these processes has advantages and disadvantages that depend on the operation conditions, the temperature of the environment and the plant capacity. Thus, for example,

- The LNG production in one train using the AP-X process varies between 5…6 and 10 MTA, whereas in one train of C3MR or DMR varies between 1…2 and 6…7 MTA, and for other processes the maximum production is up to 1.5…2 MTA.
- The LNG production per unit of power: If a maximum known value can be assumed as 100%, then the AP-X, C3MR or DMR processes are with almost 100%, the cascade processes with 90 … 80%, and the other processes with approximately 70%.
- However, the large advantage of processes with low LNG production and correspondently high energy consumption is that these processes can be used for small-scale LNG plants, especially for offshore applications.
- The specific cost values associated with the capital investment for LNG plants depend on the year of construction: For the second generation (1980s) – US$ 600/ton_LNG and for the last generation (2000s) – US$ 200/ton_LNG.

Since the beginning of the LNG history, the following types of regasification processes have been used in import terminals:

- Open-rack vaporizers using seawater. The energy consumption is approximately 0.008 kWh/kg$_{(LNG)}$ for driving the seawater circulating pumps.
- Submerged combustion vaporizers that are water baths heated by burning fuel gas. Between 1.5 and 2% of the imported gas is used as fuel gas for LNG vaporization.
- Intermediate fluid vaporizers and process integration.

The range of deviation in the total capital investment cost for the import terminals is larger than that for the export terminals. For example, the total capital investment for a small import terminal (2.0 to 2.5 million ton LNG/year) constructed in the middle of 1980s was approximately US$ 100 to 130 million, while the new generation of middle-capacity import terminals (4.0 to 8.0 million ton LNG/year) have a total capital investment of US$ 200 to 300 million. Modern technologies used for the regasification process lead to an increase in the capital investment of the import terminals up to US$ 400 million (USA, 2009-2010) and they even can be higher than US$ 2 billion for a state-of-the art Japanese import terminal with process integration technologies.

The information given in this section is based on various References, for example, [1-9].

Since 2007 a group at the Chair of Energy Engineering and Protection of the Environment at Technische Universität Berlin has been studying LNG-related technologies, mainly liquefaction and regasification processes. Using the so-called exergy-based methods, the research aims at (a) improving existing processes, (b) developing thermodynamically and economically efficient processes, and (c) conducting environmental-impact evaluations of these processes.

In this scientific area it is not possible to find an "optimal" liquefaction or regasification process; therefore, different processes must be studied and, if possible, improved from the thermodynamic and economic points of view.

2. Exergy-based methods

Exergy is defined as the maximum theoretical useful work (shaft work or electrical work) obtainable from an energy conversion system as this is brought into thermodynamic equilibrium with the thermodynamic environment while interacting only with this environment.

An *exergetic analysis* identifies the location, magnitude, and causes of thermodynamic inefficiencies, which are the *exergy destruction* (due to irreversibilities within each system component), and the *exergy loss* (exergy transfer to the environment). In an exergetic analysis, we calculate the exergy associated with each energy carrier (stream) in the

overall system, the exergy destruction within each system component and process, and the *exergetic efficiency* (for each process, component, or system) [10].

Modern exergetic analyses use the general concept of *fuel* and *product* introduced almost 30 years ago [14]): The *exergy of product* is the desired result (expressed in exergy terms) achieved by the system (e.g., the *k*th component) being considered, and the *exergy of fuel* represents the exergetic resources expended to generate the exergy of the product. These concepts are used in a consistent way in all exergy-based analyses [10-13] that include the *exergoeconomic* and the *exergoenvironmental* analyses.

The exergy balance for the overall cogeneration system is

$$\dot{E}_{F,tot} = \dot{E}_{P,tot} + \sum_k \dot{E}_{D,k} + \dot{E}_{L,tot} \tag{1}$$

and for the *k*th component

$$\dot{E}_{F,k} = \dot{E}_{P,k} + \dot{E}_{D,k} \tag{2}$$

The variables used for the conventional exergetic evaluation of the *k*th component in a system include the following:

- Exergy destruction rate that is calculated from the exergy balance
- Exergetic efficiency

$$\varepsilon_k = \frac{\dot{E}_{P,k}}{\dot{E}_{F,k}} = 1 - \frac{\dot{E}_{D,k}}{\dot{E}_{F,k}} \tag{3}$$

- Exergy destruction ratio

$$y_k = \frac{\dot{E}_{D,k}}{\dot{E}_{F,tot}} \tag{4}$$

Exergoeconomic analysis (for example, [10-12, 14]) is a unique combination of exergy analysis and cost analysis conducted at the component level, to provide the designer or operator of an energy conversion system with information crucial to the design or operation of a cost-effective system. A complete exergoeconomic analysis consists of (a) an exergetic analysis, (b) an economic analysis, and (c) an exergoeconomic evaluation.

The exergoeconomic model for an energy conversion system consists of *cost balances* written for the *k*th component, and of auxiliary equations based on the so-called P and F rules [11]. The cost balances can be written as

$$\dot{C}_{P,k} = \dot{C}_{F,k} + \dot{Z}_k \tag{5a}$$

or

$$c_{P,k}\dot{E}_{P,k} = c_{F,k}\dot{E}_{F,k} + \dot{Z}_k \tag{5b}$$

where

$$\dot{Z}_k = \dot{Z}_k^{CI} + \dot{Z}_k^{OM} \tag{6}$$

To simplify the discussion, we assume, that the contribution of $\dot{Z}_k^{OM}$ remains constant when the design changes, and, therefore, the changes in the value of $\dot{Z}_k$ are associated only with changes in the capital investment cost $\dot{Z}_k^{CI}$.

The real cost sources in an energy conversion system are (a) the capital investment (and the operating & maintenance expenses) for each component, (b) the cost of exergy destruction within each component, and (c) the cost of exergy loss from the overall system. The last two terms can be revealed only through an exergoeconomic analysis:

The cost rate associated with exergy destruction within the *k*th component is

$$\dot{C}_{D,k} = c_{F,k} \cdot \dot{E}_{D,k} \tag{7}$$

and the overall system

$$\dot{C}_{D,tot} = c_{F,tot} \cdot \sum \dot{E}_{D,k} \tag{8}$$

Life cycle assessment (LCA) is a technique for assessing the environmental aspects associated with a product over its life cycle. The LCA process consists of goal definition and scoping (defining the system under consideration), inventory analysis (identifying and quantifying the consumption and release of materials), and interpretation (evaluation of the results). Any of recently introduced indicators can be used for LCA.

In an *exergoenvironmental analysis* [12,13] the environmental impacts obtained by LCA are apportioned to the exergy streams pointing out the main system components with the highest environmental impact and possible improvements associated with these components. Finally, exergoenvironmental variables are calculated, and an exergoenvironmental evaluation is carried out.

The exergoenvironmental model for an energy conversion system consists of *environmental impact balances* written for the *k*th component and auxiliary equations based on the P- and F-rules [13]. The environmental impact balances can be written as

$$\dot{B}_{P,k} = \dot{B}_{F,k} + \left(\dot{Y}_k + \dot{B}_k^{PF} \right) \tag{9a}$$

or

$$b_{P,k} \dot{E}_{P,k} = b_{F,k} \dot{E}_{F,k} + \left(\dot{Y}_k + \dot{B}_k^{PF} \right) \tag{9b}$$

Here $\dot{Y}_k$ is the environmental impact that occurs during the three life-cycle phases: Construction, $\dot{Y}_k^{CO}$, operation & maintenance, $\dot{Y}_k^{OM}$, and disposal, $\dot{Y}_k^{DI}$ constitute the component-related environmental impact associated with the *k*th component $\dot{Y}_k$:

$$\dot{Y}_k = \dot{Y}_k^{CO} + \dot{Y}_k^{OM} + \dot{Y}_k^{DI} \tag{10}$$

To simplify the discussion, we assume that the value of $\dot{Y}_k$ is mainly associated with $\dot{Y}_k^{CO}$

To account for *pollutant formation* within the kth component, the variable $\dot{B}_k^{PF}$ [31] is used. The term $\dot{B}_k^{PF}$ is zero if no pollutants are formed within a process, i.e. for processes without a chemical reaction (compression, expansion, heat transfer, etc.).

The environmental impact associated with the exergy destruction within the *k*th component $\dot{B}_{D,k}$ is given by

$$\dot{B}_{D,k} = b_{F,k} \dot{E}_{D,k} \tag{11}$$

and within the overall system by

$$\dot{B}_{D,tot} = b_{F,tot} \cdot \sum \dot{E}_{D,k} \tag{12}$$

To identify the most important components from the viewpoint of formation of environmental impacts, the sum of environmental impacts $\left(\dot{Y}_k + \dot{B}_k^{PF} + \dot{B}_{D,k} \right)$ is used.

Advanced exergy-based methods have been developed for a more detailed and precise evaluation and a better improvement (optimization) of an exergy conversion system [12, 15-24]. With advanced methods we can also answer the following questions:

- What is the real potential for the thermodynamic improvement of the system? What part of the exergy destruction within each component can be avoided?
- What is the real potential for the cost improvement of the system? How much capital investment cost and cost of exergy destruction within each component can be avoided?
- What is the real potential for the environmental improvement of the system? How much component-related environmental impact and environmental impact associated with the exergy destruction within each component can be avoided?
- How does a thermodynamic, economic, or environmental improvement in one component affect (positively or negatively and by how much) the remaining components?

In an *advanced exergetic, exergoeconomic,* or *exergoenvironmental analysis,* the values of the most important variables (listed in the following) are split into endogenous/exogenous and avoidable/unavoidable parts:

- Exergy destruction in each (important) system component,
- Investment cost associated with such component, and
- Component-related environmental impact associated with such component,
- Cost of exergy destruction within each (important) system component, and
- Environmental impact associated with exergy destruction within such component.

This splitting assists in identifying the interactions among different components of the same system and in improving significantly the quality of the conclusions obtained from an exergetic, an exergoeconomic, or an exergoenvironmental evaluation. All publications up to date in the field of the advanced exergy-based methods are summarized and generalized in [17, 18, 24].

Endogenous exergy destruction is the part of exergy destruction within a component obtained when all other components operate ideally and the component being considered operates with the same efficiency as in the real system. The *exogenous* part of the variable is the difference between the value of the variable within the component in the real system and the endogenous part:

$$\dot{E}_{D,k} = \dot{E}_{D,k}^{EN} + \dot{E}_{D,k}^{EX} \tag{13}$$

Such a splitting reveals the interconnections among components.

The *unavoidable exergy destruction* ($\dot{E}_{D,k}^{UN}$) cannot be further reduced due to technological limitations such as availability and cost of materials and manufacturing methods. The difference between total and unavoidable exergy destruction for a component is the *avoidable* exergy destruction ($\dot{E}_{D,k}^{AV}$) that should be considered during the improvement procedure

$$\dot{E}_{D,k} = \dot{E}_{D,k}^{UN} + \dot{E}_{D,k}^{AV} \tag{14}$$

Combining the two splitting options gives analysts an opportunity to calculate

- the *avoidable endogenous exergy destruction* ($\dot{E}_{D,k}^{AV,EN}$), which can be reduced by improving the *k*th component from the exergetic point of view, and
- the *avoidable exogenous exergy destruction* ($\dot{E}_{D,k}^{AV,EX}$) that can be reduced by a structural improvement of the overall system, or by improving the efficiency of the remaining components.

This methodology can also be applied to the splitting of the values of capital investment cost and to the cost of exergy destruction as well as to component-related environmental impact and to environmental impact associated with exergy destruction.

Thus, conventional exergy-based analyses often suggest, for example, decreasing the exergy destruction within turbomachinery of a closed-cycle gas-turbine sub-system. This decrease of exergy destruction does not only increase the overall efficiency, but also simultaneously reduces both cost and environmental impact associated with the overall system.

3. Application to the chain "Natural gas – LNG – Natural gas"

The processes associated with liquefaction (Natural gas - LNG) and regasification (LNG - NG) can take place above, below or by crossing the temperature of the environment. This fact should be considered in the definition of the exergy of fuel and the exergy of product because it affects the results obtained from exergy-based methods. The splitting of the physical exergy into its thermal and mechanical parts (for a detailed overview see Refs. [17,25]) increases, in general, the accuracy of results obtained from an exergy-based evaluation. However, this splitting also significantly increases the complexity of the

exergy-based methods, because it almost doubles the number of exergy streams. We can conclude that a splitting of the physical exergy into its parts thermal and mechanical exergy is usually not necessary for power systems because all processes take place above the temperature of the environment and the pressure drops are relatively small [26], but is very important for processes that take place below the temperature of the environment or cross it. Different exergy conversion processes, where splitting of the physical exergy into its thermal and mechanical parts is required, have been presented using conventional and advanced exergy-based methods [17, 19-23]. Recently in a series of papers by Marmolejo-Correa & Gundersen [27-30] the effect of various definitions of the exergetic efficiency (including "exergy of product/exergy of fuel" with splitting the physical exergy) was reported.

General guidelines for defining the exergy of fuel and exergy of product as well as for writing the auxiliary equations to the cost balances (for the exergoeconomic analysis) are discussed in detail in Ref. [11].

Let us now discuss a hypothetical process from state 1 to state 2 taking place within a hypothetical component (Figure 1) with the incoming streams *n, p, 1,* and the outgoing streams *m, q, 2*. The following three options are possible:

- Option 1 − The process takes place entirely above the temperature of the environment, i.e. $T_1 > T_0$ and $T_2 > T_0$

- Option 2 − The process takes place across the temperature of the environment, i.e. $T_2 > T_0 > T_1$ or $T_2 \leq T_0 \leq T_1$, and

- Option 3 − The process takes place entirely below the temperature of the environment, i.e. $T_2 < T_0$ and $T_1 < T_0$.

- Only changes in the thermal exergy are considered:

- Option 1: If $\dot{E}_1^T < \dot{E}_2^T$, then the difference $\left(\dot{E}_2^T - \dot{E}_1^T \right)$ is part of the product of the component. If $\dot{E}_1^T \geq \dot{E}_2^T$, then the difference $\left(\dot{E}_1^T - \dot{E}_2^T \right)$ is part of the fuel of the component.

- Option 2: Independently of whether $\dot{E}_1^T < \dot{E}_2^T$ or $\dot{E}_1^T > \dot{E}_2^T$, the difference in thermal exergy from T_1 to T_0 should be considered as part of the fuel $\left(\dot{E}_1^T - \dot{E}_0^T \right) = \dot{E}_1^T$ because this exergy is supplied to the component, and the difference in thermal exergy from T_0 to T_2 should be considered as part of the product $\left(\dot{E}_2^T - \dot{E}_0^T \right) = \dot{E}_2^T$ because this exergy removed from the system .

- Option 3: If $\dot{E}_1^T > \dot{E}_2^T$, then the difference $\left(\dot{E}_1^T - \dot{E}_2^T \right)$ is part of the fuel for the component, whereas if $\dot{E}_1^T < \dot{E}_2^T$, then the difference $\left(\dot{E}_2^T - \dot{E}_1^T \right)$ is part of the product of the component.
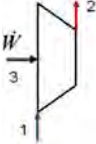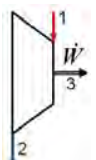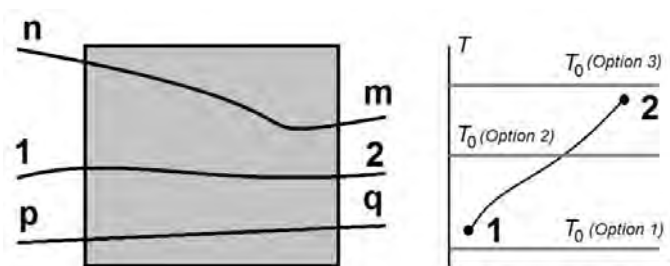
Fig. 1: *Figure used to explain options that need to be considered in defining fuel and product at different operation conditions*

Table 1: *Exergy rates associated with fuel and product, cost balances and auxiliary equations*

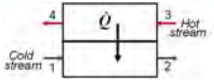| Component, schematic	Operation conditions	Exergy analysis	Cost balance	Auxiliary equations
Compressor	$T_1 > T_0$	$\dot{E}_{F,k} = \dot{E}_3 = \dot{W}_{CM}$ and $\dot{E}_{P,k} = \dot{E}_2 - \dot{E}_1$	$\dot{C}_w + \dot{Z}_{CM} = \dot{C}_2 - \dot{C}_1$	–
		$\dot{E}_{F,k} = \dot{E}_3 = \dot{W}_{CM}$ and $\dot{E}_{P,k} = \left(\dot{E}_2^T - \dot{E}_1^T\right) + \left(\dot{E}_2^M - \dot{E}_1^M\right)$	$\dot{C}_w + \dot{Z}_{CM} = \left(\dot{C}_2^T - \dot{C}_1^T\right) + \left(\dot{C}_2^M - \dot{C}_1^M\right)$	$\dfrac{\dot{C}_2^T - \dot{C}_1^T}{\dot{E}_2^T - \dot{E}_1^T} = \dfrac{\dot{C}_2^M - \dot{C}_1^M}{\dot{E}_2^M - \dot{E}_1^M}$ (P rule)
	$T_2 > T_0 > T_1$	$\dot{E}_{F,k} = \dot{W}_{CM} + \dot{E}_1^T$ and $\dot{E}_{P,k} = \dot{E}_2^T + \left(\dot{E}_2^M - \dot{E}_1^M\right)$	$\dot{C}_1^T + \dot{C}_w + \dot{Z}_{CM} = \dot{C}_2^T + \left(\dot{C}_2^M - \dot{C}_1^M\right)$	$\dfrac{\dot{C}_2^T}{\dot{E}_2^T} = \dfrac{\dot{C}_2^M - \dot{C}_1^M}{\dot{E}_2^M - \dot{E}_1^M}$ (P rule)
	$T_2 < T_0$	$\dot{E}_{F,k} = \dot{W}_{CM} + \left(\dot{E}_1^T - \dot{E}_2^T\right)$ and $\dot{E}_{P,k} = \left(\dot{E}_2^M - \dot{E}_1^M\right)$	$\left(\dot{C}_2^T - \dot{C}_1^T\right) + \dot{C}_w + \dot{Z}_{CM} = \left(\dot{C}_2^M - \dot{C}_1^M\right)$	$\dfrac{\dot{C}_2^T}{\dot{E}_2^T} = \dfrac{\dot{C}_1^T}{\dot{E}_1^T}$ (P rule)
Turbine	$T_1 > T_0$	$\dot{E}_{F,k} = \dot{E}_1 - \dot{E}_2$ and $\dot{E}_{P,k} = \dot{E}_3 = \dot{W}_T$	$\left(\dot{C}_2 - \dot{C}_1\right) + \dot{Z}_T = \dot{C}_w$	$\dfrac{\dot{C}_2}{\dot{E}_2} = \dfrac{\dot{C}_1}{\dot{E}_1}$
	$T_2 > T_0 > T_1$	$\dot{E}_{F,k} = \left(\dot{E}_1^M - \dot{E}_2^M\right) + \dot{E}_1^T$ and $\dot{E}_{P,k} = \dot{E}_2^T + \dot{W}_T$	$\dot{C}_1^T + \left(\dot{C}_1^M - \dot{C}_2^M\right) + \dot{Z}_T = \dot{C}_2^T + \dot{C}_w$	$\dfrac{\dot{C}_2^M}{\dot{E}_2^M} = \dfrac{\dot{C}_1^M}{\dot{E}_1^M}$ (P rule) $\dfrac{\dot{C}_2^T}{\dot{E}_2^T} = \dfrac{\dot{C}_w}{\dot{W}_T}$ (F rule)
	$T_2 < T_0$	$\dot{E}_{F,k} = \dot{E}_1^M - \dot{E}_2^M$ and $\dot{E}_{P,k} = \dot{E}_2^T - \dot{E}_1^T$	$\left(\dot{C}_1^M - \dot{C}_2^M\right) + \dot{Z}_T = \left(\dot{C}_2^T - \dot{C}_1^T\right) + \dot{C}_w$	$\dfrac{\dot{C}_2^M}{\dot{E}_2^M} = \dfrac{\dot{C}_1^M}{\dot{E}_1^M}$ (P rule) $\dfrac{\dot{C}_2^T - \dot{C}_1^T}{\dot{E}_2^T - \dot{E}_1^T} = \dfrac{\dot{C}_w}{\dot{W}_T}$ (F rule)
Throttling valve	$T_1 > T_0$	Dissipative component, $\dot{E}_{D,TV} = \dot{E}_1 - \dot{E}_2$	$\dot{C}_1 + \dot{Z}_{TV} = \dot{C}_2 + \delta\dot{C}_{TV}$ (assumption for the dissipative components [11])	$\dfrac{\dot{C}_2}{\dot{E}_2} = \dfrac{\dot{C}_1}{\dot{E}_1}$
	$T_2 > T_0 > T_1$	$\dot{E}_{F,k} = \left(\dot{E}_1^M - \dot{E}_2^M\right) + \dot{E}_1^T$ and $\dot{E}_{P,k} = \dot{E}_2^T$	$\dot{C}_1^T + \left(\dot{C}_1^M - \dot{C}_2^M\right) + \dot{Z}_{TV} = \dot{C}_2^T$	$\dfrac{\dot{C}_2^M}{\dot{E}_2^M} = \dfrac{\dot{C}_1^M}{\dot{E}_1^M}$ (P rule)
	$T_2 < T_0$	$\dot{E}_{F,k} = \dot{E}_1^M - \dot{E}_2^M$ and $\dot{E}_{P,k} = \dot{E}_2^T - \dot{E}_1^T$	$\left(\dot{C}_1^M - \dot{C}_2^M\right) + \dot{Z}_{TV} = \left(\dot{C}_2^T - \dot{C}_1^T\right)$	$\dfrac{\dot{C}_2^M}{\dot{E}_2^M} = \dfrac{\dot{C}_1^M}{\dot{E}_1^M}$ (P rule)

Component, schematic	Operation conditions	Exergy analysis	Cost balance	Auxiliary equations
Heat exchanger	$T_1 > T_0$	$\dot{E}_{F,k} = \dot{E}_3 - \dot{E}_4$ and $\dot{E}_{P,k} = \dot{E}_2 - \dot{E}_1$	$\left(\dot{C}_3 - \dot{C}_4\right) + \dot{Z}_{HE} = \left(\dot{C}_2 - \dot{C}_1\right)$	$\dfrac{\dot{C}_3}{\dot{E}_3} = \dfrac{\dot{C}_4}{\dot{E}_4}$ (F rule)
	$T_1 < T_0$, $T_2 < T_0$, $T_4 < T_0$ and $T_3 > T_0$	$\dot{E}_{F,k} = \left(\dot{E}_1^M - \dot{E}_2^M\right) +$ $\left(\dot{E}_3^M - \dot{E}_4^M\right) + \left(\dot{E}_1^T - \dot{E}_2^T\right) + \dot{E}_3^T$ and $\dot{E}_{P,k} = \dot{E}_4^T$	$\left(\dot{C}_1^M - \dot{C}_2^M\right) + \left(\dot{C}_3^M - \dot{C}_4^M\right) +$ $\left(\dot{C}_1^T - \dot{C}_2^T\right) + \dot{C}_3^T + \dot{Z}_{HE} = \dot{C}_4^T$	$\dfrac{\dot{C}_2^M}{\dot{E}_2^M} = \dfrac{\dot{C}_1^M}{\dot{E}_1^M}$ (F rule) $\dfrac{\dot{C}_3^M}{\dot{E}_3^M} = \dfrac{\dot{C}_4^M}{\dot{E}_4^M}$ (F rule) $\dfrac{\dot{C}_1^T}{\dot{E}_1^T} = \dfrac{\dot{C}_2^T}{\dot{E}_2^T}$ (F rule)
	$T_1 < T_0$ and $T_2 < T_0$ $T_3 > T_0$ and $T_4 > T_0$	Dissipative component, $\dot{E}_{D,HE} = \left(\dot{E}_1 - \dot{E}_3\right) - \left(\dot{E}_2 - \dot{E}_4\right)$	$\dot{C}_1 + \dot{C}_3 + \dot{Z}_{HE} = \dot{C}_2 + \dot{C}_4 + \delta\dot{C}_{HE}$ (assumption for the dissipative components [11])	$\dfrac{\dot{C}_2}{\dot{E}_2} = \dfrac{\dot{C}_1}{\dot{E}_1}$ or $\dfrac{\dot{C}_3}{\dot{E}_3} = \dfrac{\dot{C}_4}{\dot{E}_4}$
	$T_1 < T_0$ and $T_2 > T_0$, $T_3 > T_0$, $T_4 > T_0$	$\dot{E}_{F,k} = \left(\dot{E}_1^M - \dot{E}_2^M\right) +$ $\left(\dot{E}_3^M - \dot{E}_4^M\right) + \left(\dot{E}_3^T - \dot{E}_4^T\right) + \dot{E}_1^T$ and $\dot{E}_{P,k} = \dot{E}_2^T$	$\left(\dot{C}_1^M - \dot{C}_2^M\right) + \left(\dot{C}_3^M - \dot{C}_4^M\right) +$ $\left(\dot{C}_3^T - \dot{C}_4^T\right) + \dot{C}_1^T + \dot{Z}_{HE} = \dot{C}_2^T$	$\dfrac{\dot{C}_2^M}{\dot{E}_2^M} = \dfrac{\dot{C}_1^M}{\dot{E}_1^M}$ (F rule) $\dfrac{\dot{C}_3^M}{\dot{E}_3^M} = \dfrac{\dot{C}_4^M}{\dot{E}_4^M}$ (F rule) $\dfrac{\dot{C}_3^T}{\dot{E}_3^T} = \dfrac{\dot{C}_4^T}{\dot{E}_4^T}$ (F rule)
	$T_3 < T_0$	$\dot{E}_{F,k} = \left(\dot{E}_1^M - \dot{E}_2^M\right) +$ $\left(\dot{E}_3^M - \dot{E}_4^M\right) + \left(\dot{E}_1^T - \dot{E}_2^T\right)$ and $\dot{E}_{P,k} = \dot{E}_3^T - \dot{E}_4^T$	$\left(\dot{C}_1^M - \dot{C}_2^M\right) + \left(\dot{C}_3^M - \dot{C}_4^M\right) +$ $+ \left(\dot{C}_1^T - \dot{C}_2^T\right) + \dot{Z}_{HE} = \left(\dot{C}_3^T - \dot{C}_4^T\right)$	$\dfrac{\dot{C}_2^M}{\dot{E}_2^M} = \dfrac{\dot{C}_1^M}{\dot{E}_1^M}$ (F rule) $\dfrac{\dot{C}_3^M}{\dot{E}_3^M} = \dfrac{\dot{C}_4^M}{\dot{E}_4^M}$ (F rule) $\dfrac{\dot{C}_1^T}{\dot{E}_1^T} = \dfrac{\dot{C}_2^T}{\dot{E}_2^T}$ (F rule)

Table 1 presents the equations for the main components (compressor, expander, throttling valve and two-flow heat exchanger) of a low-temperature energy conversion system under different operation conditions (above, below or crossing the temperature of the environment). Note that when an expander or a throttling valve operates across or below the temperature of the environment, the purpose of such a component is to produce low-temperature thermal exergy (temperature at state 2, Table 1).

The cost balances and auxiliary equations developed for the exergoeconomic analysis can be easily converted to environmental impact balances and auxiliary equations for the exergoenvironmental analysis [13].

Splitting the exergy destruction in its thermal and mechanical parts affects (a) the value of the exergetic efficiency of the *k*th component, and (b) the costs associated with thermal and mechanical exergy streams. It is fair to say that conclusions obtained from such an exergy-based analysis are more precise.

4. Conclusions

Advanced exergy-based methods help us to deeply understand an energy conversion processes, and more specifically the interactions among system components, and the real potential for improving each component and the overall system.

This paper demonstrates that for the evaluation of the processes within the chain "NG-LNG-NG", the exergy-based methods should be applied in conjunction with a splitting of the physical exergy into its thermal and mechanical exergy parts. Despite additional complexity, the obtained results provide us with more precise information about the value of the exergetic efficiency of the *k*th component, and the cost (environmental impact) associated with thermal and mechanical exergy streams. Thus, based on this information, we can develop more precise conclusions for the improvement of the overall system.

References

[1]. WORLD LNG REPORT 2010 (www.petronas.com).

[2]. J.C. Bronfenbrenner, M. Pillarella M. & J. Solomon, "Review the process technology options available for the liquefaction of natural gas", Air products and chemicals, Inc., USA, 2009, (www.lngindustry.com).

[3]. EUROGAS, "Natural Gas Demand and Supply. Long term Outlook to 2030" (www.eurogas.com).

[4]. International Gas Union, "PFC Energy. World LNG Report 2010. News, views and knowledge on gas – worldwide" (www.petronas.com).

[5]. GIIGNL, "The LNG industry 2010", International Group of Liquefied Natural Gas Importers, (http://www.giignl.org).

[6]. International Institute of Refrigeration, "Liquefied Natural Gas: Current Expansion and Perspectives". *19-th Informatory Note on Refrigerating Technologies.* International Institute of Refrigeration, Paris, France, (http://www.iifiir.org).

[7]. US department of Energy (www.eia.doe.gov).

[8]. World LNG report 2010 (www.petronas.com).

[9]. LNG Price Assessments. Platts Daily Spot, LNG FAQ (http://www.platts.com).

[10]. A. Bejan, G. Tsatsaronis & M. Moran, "Thermal Design and Optimization" (John Wiley & Sons, 1996).

[11]. A. Lazzaretto & G. Tsatsaronis, *Energy*, 31 (2006) 1257–1289.

[12]. G. Tsatsaronis, *International Journal of Exergy*, 5 (2008) 489–499.

[13]. L.Meyer, G. Tsatsaronis, J. Buchgeister & L. Schebek, L. *Energy Int. J.*, 34 (2009) 75-89.

[14]. G. Tsatsaronis, "Combination of Exergetic and Economic Analysis in Energy-Conversion Processes" in *Energy Economics and Management in Industry*, Proceedings of the European Congress, Algarve, Portugal, April 2-5, 1984 (England, Oxford: Pergamon Press), Vol. 1, 151-157.

[15]. G. Tsatsaronis, "Strengths and limitations of exergy analysis" in *Thermodynamic optimization of complex energy systems* (eds.) A. Bejan & E. Mamut (Dordrecht: Kluwer Academic Publishers) 93–100.

[16]. G. Tsatsaronis & M.H. Park, *Energy Conversion and Management*, 43 (2002) 1259-1270.

[17]. T. Morosuk & G. Tsatsaronis, Energy, 33 (2008) 890-907.

[18]. G. Tsatsaronis & T. Morosuk, "A general exergy-based method for combining a cost analysis with an environmental impact analysis" in *Proceedings of the ASME international mechanical engineering congress and exposition*, Boston, MA: USA, files IMECE2008-67218 and IMECE2008-67219.

[19]. S. Kelly, G. Tsatsaronis & T. Morosuk, *Energy*, Vol. 34 (2009) 384-391.

[20]. G. Tsatsaronis & T. Morosuk, *Energy*, 35 (2010) 820-829.

[21]. T. Morosuk & G. Tsatsaronis, *Energy*, 36 (2011) 3771-3778.

[22]. T. Morosuk & G. Tsatsaronis, "LNG – Based Cogeneration Systems: Evaluation Using Exergy-Based Analyses" in *Natural Gas - Extraction to End Use* (eds.) S.B. Gupta (InTech, 2012) 235-266.

[23]. T. Morosuk, G. Tsatsaronis, A. Boyano & C. Gantiva, *International Journal of Energy and Environmental Engineering* 3:1 (2012) (http://www.journal-ijeee.com/content/3/1/1).

[24]. G. Tsatsaronis & T. Morosuk T, *International Journal of Exergy*, 11 (2012) 518–542.

[25]. T. Morosuk & G. Tsatsaronis, "Graphical Models for Splitting Physical Exergy" in *Shaping our future energy systems*, Proceedings of the 18th International Conference on Efficiency, Costs, Optimization, Simulation and Environmental Impact of Energy Systems, ECOS 2005 (eds.) S. Kjelstrup et al., Trondheim, Norway, June 20-22, 2005, 377-384.

[26]. B. Erlach, G. Tsatsaronis & F. Cziesla, *International Journal of Applied Thermodynamics*, 4 (2001) 145-156.

[27]. D. Marmolejo-Correa & T. Gundersen, *Computer Aided Chemical Engineering*, 31 (2012) 1180-1184.

[28]. D. Marmolejo-Correa & T. Gundersen, *Energy*, 44 (2012) 477-489.

[29]. D. Marmolejo-Correa & T. Gundersen, Computer Aided Chemical Engineering, 29 (2011) 1909-1913.

[30]. D. Marmolejo-Correa & T. Gundersen, Computer Aided Chemical Engineering, 30 (2012) 557-561.

[31]. A. Boyano, A.M. Blanco, T. Morosuk, and G. Tsatsaronis, *Energy*, 36 (2011) 2202-2214.

LIFE CYCLE MANAGEMENT OF LOW-CARBON BUILDING MATERIALS FOR SMART CITIES

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1. Introduction

Some key drivers for implementation of low carbon technologies in the built environment for smart cities are:

- applying carbon neutral building materials obtained from renewable resources,
- incorporating re-use of building products or re-cycling of building materials,
- using renewable energy sources for heat and electricity in buildings, or
- improving energy performance and reducing energy demand in buildings regards electricity and heating.

However, low carbon, highly insulated and most energy-efficient buildings (passive houses) are not the only important elements. Other aspects should be taken into account such as:

- light- and thermal comfort and excellent indoor air quality,
- potential fire risks,
- materials should be disposable/recyclable without causing harm, and most important
- building materials should not contain questionable chemicals which somewhere in the life cycle could be released to the indoor- and outdoor environment and expose wildlife or humans.

An example of an aspect often overlooked is use of hazardous chemicals as flame retardant in flammable building materials in order to reduce a fire risk. Such flame retardants have a limited ability to prevent a fire ignited by a strong source and can give a false sense of safety. The smoke released at such a fire may also be more toxic. The content of flame retardants may also make recycling, useless, difficult or impossible and in some instances illegal. Examples of building materials which normally need flame retardant to comply with fire regulations are:

- paper wool insulation using the flame retardant, boric acid/borates, which in REACH are a substance of very high concern and classified as toxic to reproduction, or
- polyurethane (PUR/PIR) insulation using a chlorinated organophosphates, which in REACH also are a substance of very high concern and classified as toxic to reproduction etc., and modern us of PUR spray insulation has also had a health issue. In the Netherlands more than 130 people have recently been sick living in

houses where the basement is sprayed with 2 C polyurethane. Remarkable was that baby's and small children had more heavy health symptoms then grown up's, fever > 40°C, rash over the whole body etc.

- polystyrene (EPS/XPS) insulation and outer walls using hexabromocyclododecane (HBCDD) as the only flame retardant. In REACH HBCDD is also are a substance of very high concern and classified as toxic to reproduction, and HBCDD has recently been listed in Annex A of the Stockholm Convention and has to be phased out. But the content of HBCDD makes it illegal to recycle most of the EPS/XPS, when existing buildings are demolished.

If smart cities shall be really smart, it is necessary to take all relevant factors in the materials life cycle into account and not only low carbon. Applying life cycle thinking/management is necessary to get that overview over all aspects in the life cycle. I the following HBCDD will be discussed.

2. HBCDD case

Hexabromocyclododecane (HBCDD or HBCD) is an ever-more prevalent chemical that is used mainly as a flame retardant in polystyrene-based building insulation products. It is a lipophilic and persistent organic pollutant (POP), which bioaccumulates in organisms and biomagnifies through the food chain; this leads to progressively increasing background levels in wildlife and ultimately in human tissues. The extent of this accumulation correlates directly with its ever-more prevalent use.

In 2008, The European Union published a comprehensive risk assessment of HBCDD (EU 2008), and the Nordic Council of Ministers published a general review of HBCDD (NM 2008). In the same year, the European Chemicals Agency (ECHA 2008) identified HBCDD as 1 of 14 substances of "Very High Concern", and in September 2010 HBCDD was added to the Authorisation List in the European Union Registration Evaluation Authorisation and restriction of Chemicals (REACH) regulations.

HBCDD was included in the 'San Antonio Statement on Brominated and Chlorinated Flame Retardants' signed in September 2010 by 245 scientists from 22 countries warning about the adverse effects of these substances (DiGangi *et al.* 2010).

In February 2011, the ECHA (ECHA 2011) selected HBCDD to be phased out before 2015, if authorization is not granted to potential applicants before the "last application date".

In 2011 the European Food Safety Agency (EFSA) published a *Scientific Opinion on Hexabromocyclododecanes (HBCDDs) in Food* (EFSA 2011). This concluded that the derivation of health-based guidance values for HBCDDs was not appropriate because of the limitations and uncertainties in the database.

In May 2013 HBCDD was listed in Annex A of the the Stockholm Convention and a global ban of HBCDD use has to be enforced in 18 months (Stockholm Convention 2013).

3. What is HBCDD?

Commercial HBCDD products with Chemical Abstract Service (CAS) No's 25637-99-4 or 3194-55-6 are a racemic mixture of mainly three isomers: (i) α-HBCDD; (ii) β-HBCDD and (iii) γ-HBCDD. Figure 1 shows their structure and approximate composition:
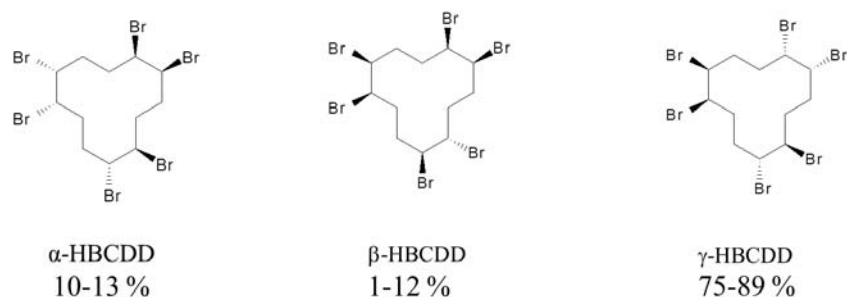

α-HBCDD
10-13 %

β-HBCDD
1-12 %

γ-HBCDD
75-89 %

Fig. 1: Chemical structures of the three main HBCDD (hexabromocyclododecane) isomers.

The single isomers have slightly different physicochemical characteristics: α-HBCDD is the most thermodynamically stable isomer.

The HBCDD mixture is characterized by very poor water solubility (66 µg/L at 20°C), high lipophilicity (Log K_{ow}: 5.6), low volatility (6×10^{-5} Pa at 21°C) and a melting point of 190°C.

HBCDD has been used increasingly as a substitute for other brominated flame retardants, such as polybrominated diphenyl ethers (PBDEs). Worldwide production has grown from 16 000 tons in 2000 to 23 000 tons in 2008; a significant portion of this increase has occurred in China (Klif 2011).

An estimated 80% of HBCDD produced is utilized as a flame retardant in expanded and extruded polystyrene (EPS/XPS) insulation products that are used for building and construction. In addition, HBCDD is applied to high impact polystyrene (HIPS) in electrical or electronic parts. It is also used in polymer-dispersion coating agents found in textiles for upholstery fabric, furniture, mattress ticking and for seating in vehicles (EU 2008).

EPS/XPS products are relatively cheap and energy-efficient materials that are easy to work with. It is estimated that they accounts for 35% of building insulation in Europe and now it is also used as wall material. Many EPS/XPS producers are located in Eastern Europe, where these materials have a large market. Since these insulation materials consist of 90% air, and therefore have a relatively large volume, only short distribution distances are economically viable. As a result, instead of a few large producers, production is geographically spread, and most producers are small to medium enterprises. Such enterprises are important for the indigenous business: thus, the closing-down of these businesses would have a significant impact on local economies.

Table 1: Emissions of hexabromocyclododecane (HBCDD) in Europe.

Life-cycle stage	Total HBCDD emissions in Europe (kg/year)		
	Air	Waste water	Surface water
Production	2.0	0.7	0
Micronizing	0.3	0	0
Formulation of EPS and HIPS	20	48	*212*
Formulation of XPS	11	71	8.5
Formulation polymer dispersion	6.8	*220*	55
Industrial use EPS	*102*	82	20
Industrial use HIPS	6.3	5.0	1.3
Industrial use XPS (compound)	*100*	27	7
Industrial use XPS (powder)	24	26	6.6
Industrial use textile back coating	0.6	*5653*	*1413*
Insulation boards, professional use	*182*	*0*	*182*
Service life textiles (washing)	0	10	0
Service life textiles (wear)	0	107	27
Service life EPS/XPS	54	0	0
Total emissions	**508**	**6251**	**1933**

Source: EU 2008. EPS = expanded polystyrene; HIPS = high impact polystyrenes; XPS = extruded polystyrene.

Figures in italics are the most important emissions.

Table 1 provides estimates of HBCDD emissions in Europe from an EU Risk Assessment Report (EU 2008). This shows that air emissions are derived mainly from industrial use and installation boards, whereas water emissions originate primarily in the textile industry. However, this assessment does not give a complete picture as it did not examine indoor or terrestrial environmental emissions. Neither did it look at life cycle stages of waste and recycling. Buildings have a typical lifespan of more than 50 years: on demolition, it will be necessary to collect and dispose of insulation boards safely to avoid emission into the environment.

Even though HBCDD is used as a substitute for polybrominated diphenyl ethers (PBDEs) in the electronics industry, neither were emissions from this source considered. However, recent studies of an electronic waste facility in China showed that it had polluted the surrounding areas with 1.8 tons of HBCDD, and that HBCDD levels in the soil at a distance of 50 km from the plant had increased (Gao *et al.* 2011).

4. HBCDD in wildlife and humans

Trend studies of HBCDD in lake sediments have shown rising levels since the beginning of the 1980s (Kohler *et al.* 2008). In about the same period, background levels of HBCDD (mainly α-isomer) were also shown to have increased in wildlife (Vorkamp *et al.* 2011; Johansson *et al.* 2011). In areas where high levels have been recorded, a concomitant decrease has been observed following the closure of local production facilities (Law *et al.* 2008).

Human exposures are derived from work places or through food intake. However, exposure to indoor air and dust may sometimes be of more importance (Roosens *et al.* 2009).

HBCDD is absorbed into the body through the respiratory and gastrointestinal tracts and accumulates in body fats. Levels in humans are often monitored by analyzing samples of blood or human milk. Figure 2 shows that HBCDD concentrations in Swedish mothers' milk display an increasing trend over a 30-year period.
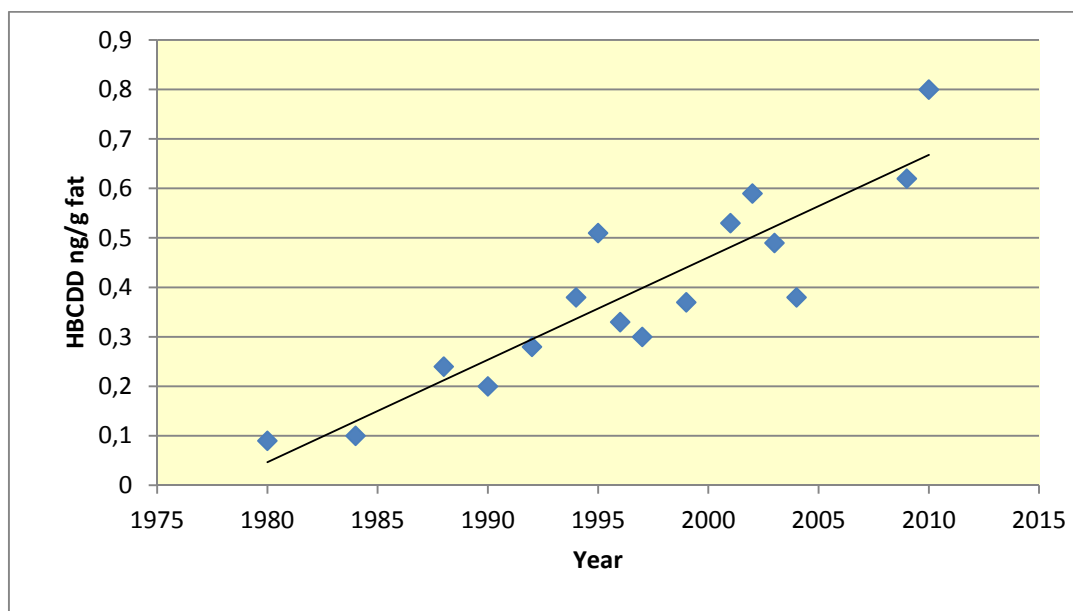

Fig, 2. Time trend of HBCDD concentration in Swedish mothers' milk (Fängström et al. 2008; EFSA 2011).

Exposure to HBCDD can have wide-ranging and potentially severe effects – particularly to the neuroendocrine system and to offspring during the early phases of development. In a two-generation rat study on HBCDD's impact on reproduction, thyroid effects were observed both in dams and offspring (Ema *et al.* 2008). The no-observable-adverse-effect-level (NOAEL) in that study was estimated to be 10 mg/kg per day.

Another study indicated that neonatal HBCDD exposure may cause statistically significant changes in spontaneous behavior and learning, and this may also induce memory defects in rats. An indicative lowest-observable-adverse-effect-level (LOAEL) of 0.9 mg/kg per day was deduced from this study (Eriksson *et al.* 2006).

HBCDD has a very low acute toxicity in animals by oral and dermal routes of administration. Its main effects are the induction of biotransformation processes (cytochrome P450 and Phase II enzymes) in the liver, which are responsible for the metabolism of drugs and many endogenous substances such as steroids and hormones. The most consistent effect found in repeated dosing in rats was a dose-dependent increase in liver weight. A NOAEL of 22.9 mg/kg per day was estimated for this effect in female rats. Pituitary and thyroid weight also increased significantly, accompanied by thyroid follicular cell hypertrophy. This effect on the pituitary induces increased the synthesis of thyroid-stimulating hormone (TSH).

HBCDD continues to be used extensively also in building considered to be green even though:

> ➢ Flammable insulation materials made from renewable sources and with less dangerous flame retardants exist.

> ➢ Non-flammable insulation alternatives are available – such as mineral wool (stone wool and glass wool), foam glass, aerogel and perlite which do not require the use of flame retardants.

> ➢ Safer chemical flame retardant alternatives to HBCDD for EPS/XPS may also be available.

5. CONCLUSIONS

The use of polystyrene insulation with HBCDD is increasing, although alternatives exist. The available information indicates that HBCDD is a dangerous substance. It is persistent, bioaccumulative and toxic. Levels of HBCDD are generally increasing in both the environment and in humans. For these reasons, the regulations of HBCDD by ECHA and the Stockholm Convention are both correct and timely! And using EPS with HBCDD for smart cities is not very smart but problematic.

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References

[1]. DiGangi J., Blum A., Bergman Å., de Wit C.A., Lucas D., Mortimer D., Schecter A., Scheringer M., Shaw S.D. and Webster T.F. 2010. Editorial: San Antonio Statement on Brominated and Chlorinated Flame Retardants. *Environ. Health Perspec.*, 118, A516–18.

[2]. Ema M., Fujii S., Hirata-Koizumi M. and Matsumoto M. 2008. Two-generation reproductive toxicity study of the flame retardant hexabromocyclododecane in rats. *Reprod. Toxicol.*, 25, 335–51.

[3]. EFSA Panel on Contaminants in the Food Chain (CONTAM). Scientific Opinion on Hexabromocyclododecanes (HBCDDs) in Food. EFSA Journal 2011;9(7):2296

[4]. Eriksson P., Fisher C., Wallin M., Jakobsson E. and Fredriksson A. 2006. Impaired behaviour, learning and memory, in adult mice neonatally exposed to hexabromocyclododecane (HBCDD). *Environ. Toxicol. Pharmacol.*, 21, 317–22.

[5]. European Chemicals Agency (ECHA) 2011. http://ECHA.europe.eu

[6]. European Union (EU). 2008. *Risk Assessment Report on Hexabromocyclododecane, CAS-No. 25637-99-4*. Final draft May 2008. http://ecb.jrc.ec.europa.eu/

[7]. Fängström B., Athanassiadis I., Odsjö T., Norén K. and Bergman Å. 2008. Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in milk from Stockholm mothers, 1980–2004. *Mol. Nutr. Food Res.*, 52, 187–93.

[8]. Gao S., Wang J., Yu Z., Guo Q., Sheng G. and Fu J. 2011. Hexabromocyclododecanes in surface soils from E-waste recycling areas and industrial areas in South China: concentrations, diastereoisomer- and enantiomer-specific profiles, and inventory. *Environ. Sci. Technol.,* 45, 2093–9.

[9]. Johansson A.-K., Sellström U., Lindberg P., Bignert A. and De Witt C.A. 2011. Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in Swedish Perigrine Falcon (*Falco perigrinus perigrinus*) eggs. *Environ. Int.*, 37, 678–86.

[10]. Klif. 2011. *Alternatives to the use of flame retarded EPS*. TA-2827. http://www.klif.no/no/Publikasjoner/Publikasjoner/2011/Juli/Alternatives-to-the-use-of-flame-retarded-EPS/

[11]. Law R.J., Bersuder P., Brady J., Wilford B.H., Allchin C.R. and Jepson P.D. 2008. A significant downturn in levels of hexabromocyclododecane in the blubber of harbour porpoise (*Phocoena Phocoena*) stranded or caught in the UK: an update to 2006. *Environ. Sci. Technol.*, 42, 9104–9.

[12]. Nordic Council of Ministers (NM). 2008. *Hexabromocyclododecane as a possible global POP*. TemaNord. Copenhagen, Denmark.

[13]. Roosens L., Abdallah M.A.-E., Harrad S., Neels H. and Covaci A. 2009. Exposure to hexabromocyclododecanes (HBCDs) via dust ingestion, but not diet, correlates with concentrations in human serum: preliminary results. *Environ. Health Perspec.*, 117, 1707–12.

[14]. Stockholm Convention. 2013. http://chm.pops.int/

[15]. Vorkamp K., Rigét F.F., Bossi R. and Dietz R. 2011. Temporal trends of hexabromocyclododecane, polybrominated diphenyl ethers and polychlorinated biphenyls in ringed seals from East Greenland. *Environ. Sci. Technol.*, 45, 1243–9.

ENERGY GENERATING BUILDING ENVELOPES

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Abstract

This paper discusses the potential for generating energy, using building integrated thermal and electrical renewable energy systems. The paper first reviews the energy generating potential of building envelopes in relation to their micro-climate environments. It provides some case study examples from practice, including the Sustainable Building Envelop Centre (SBEC) which is part of the Welsh Low Carbon Research Institute (LCRI). The main focus will be on solar radiation, although wind will also be considered. The paper then considers the performance of emerging technologies and products related to energy generating building envelope components, for example, the transpired solar air collector, and solar PV cladding systems. Finally, the integration of these components into a whole building system, linking the renewable energy supply to energy demand and storage will be considered, for thermal and electrical energy use, as part of a future "smart living". the scenario.

Keywords: Smart-ER; Building Envelopes; micro-climate; LCR Institute