Important Thermodynamic Concept

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***Abstract*— In this paper about the important concept of thermodynamic as exergy, entropy, first and second law of thermodynamic, industrial ecology and their application has been discussed. In thermodynamics, the exergy of a system is the maximum useful work possible during a process that brings the system into equilibrium with a heat reservoir and entropy is a thermodynamic property that can be used to determine the energy available for useful work in a thermodynamic process, such as in energy conversion devices, engines, or machines. The first law of thermodynamics states that energy cannot be created or destroyed and the second law of thermodynamics is an expression of the tendency that over time, differences in temperature, pressure, and chemical potential equilibrate in an isolated physical system. Industrial Ecology (IE) is the study of material and energy flows through industrial systems. The global industrial economy can be modeled as a network of industrial processes that extract resources from the Earth and transform those resources into commodities which can be bought and sold to meet the needs of humanity. Industrial ecology seeks to quantify the material flows and document the industrial processes that make modern society function.**

***Keywords*–** Thermodynamic, Concept, Exergy and Industrial Ecology

I. INTRODUCTION

In thermodynamics, the exergy of a system is the maximum useful work possible during a process that brings the system into equilibrium with a heat reservoir [1]. When the surroundings are the reservoir, exergy is the potential of a system to cause a change as it achieves equilibrium with its environment. Exergy is the energy that is available to be used. After the system and surroundings reach equilibrium, the exergy is zero. Determining exergy was also the first goal of thermodynamics. Energy is never destroyed during a process; it changes from one form to another (*see First Law of Thermodynamics*). In contrast, exergy accounts for the irreversibility of a process due to increase in entropy (*see Second Law of Thermodynamics*). Exergy is always destroyed when a process involves a temperature change. This destruction is proportional to the entropy increase of the system together with its surroundings. The destroyed exergy has been called anergy [1].

For an isothermal process, exergy and energy are interchangeable terms, and there is no anergy. Exergy analysis is performed in the field of industrial ecology to use energy more efficiently. The term was coined by Zoran Rant in 1956 but the concept was developed by J. Willard Gibbs in 1873 Ecologists and design engineers often choose a *reference state* for the reservoir that may be different from the actual surroundings of the system. Exergy is a combination property of a system and its environment because unlike energy it depends on the state of both the system and environment. The exergy of a system in equilibrium with the environment is zero. Exergy is neither a thermodynamic property of matter nor a thermodynamic potential of a system. Exergy and energy both have units of joules. The Internal Energy of a system is always measured from a fixed reference state and is therefore always a state function. Some authors define the exergy of the system to be changed when the environment changes, in which case it is not a state function. Other writers prefer a slightly alternate definition of the available energy or exergy of a system where the environment is firmly defined, as an unchangeable absolute reference state, and in this alternate definition exergy becomes a property of the state of the system alone. The term exergy is also used, by analogy with its physical definition, in information theory related to reversible computing. Exergy is also synonymous with: availability, available energy, exergic energy, essergy (considered archaic), utilizable energy, available useful work, maximum (or minimum) work, maximum (or minimum) work content, reversible work, and ideal work. Summaries of the evolution of exergy analysis are provided at [2-16].

II. ENTROPY

Entropy is a thermodynamic property that can be used to determine the energy available for useful work in a thermodynamic process, such as in energy conversion devices, engines, or machines. Such devices can only be driven by convertible energy, and have a theoretical maximum efficiency when converting energy to work. During this work, entropy accumulates in the system, which then dissipates in the form of waste heat. In classical thermodynamics, the concept of entropy is defined phenomenologically by the second law of thermodynamics, which states that the entropy of an isolated system always increases or remains constant. Thus, entropy is also a measure of the tendency of a process, such as a chemical reaction, to be entropically favored, or to proceed in a particular direction. It determines that thermal energy always flows spontaneously from regions of higher temperature to regions of lower temperature, in the form of heat. These processes reduce the state of order of the initial systems, and therefore entropy is an expression of disorder or randomness. This picture is the basis of the modern microscopic interpretation of entropy in statistical mechanics, where entropy is defined as the amount of additional information needed to specify the exact physical state of a system, given its thermodynamic specification. The second law is then a consequence of this definition and the fundamental postulate of statistical mechanics. Thermodynamic entropy has the dimension of energy divided by temperature, and a unit of joules per kelvin (J/K) in the International System of Units.

III. FIRST LAW OF THERMODYNAMICS

The *first law of thermodynamics* states that energy cannot be created or destroyed. It is often expressed by the statement that in a thermodynamic process the increment in the internal energy of a system is equal to the increment of heat supplied to the system, minus the increment of work done by the system on its surroundings. The first law of thermodynamics observes the principle of conservation of energy. Energy can be transformed, i.e. changed from one form to another, but cannot be created nor destroyed. The first explicit statement of the first law of thermodynamics referred to cyclic thermodynamic processes. It was made by Rudolf Clausius in 1850:

In all cases in which work is produced by the agency of heat, a quantity of heat is consumed which is proportional to the work done; and conversely, by the expenditure of an equal quantity of work an equal quantity of heat is produced.

Clausius stated the law also in another form, this time referring to the existence of a function of state of the system called the internal energy, and expressing himself in terms of a differential equation for the increments of a thermodynamic process. This equation may be translated into words as follows:

In a thermodynamic process, the increment in the internal energy of a system is equal to the difference between the increment of heat accumulated by the system and the increment of work done by it.

A. Description

The first law of thermodynamics was expressed in two ways by Clausius. One way referred to cyclic processes and the inputs and outputs of the system, but did not refer to increments in the internal state of the system. The other way referred to any incremental change in the internal state of the system, and did not expect the process to be cyclic. A cyclic process is one which can be repeated indefinitely often and still eventually leave the system in its original state.

In each repetition of a cyclic process, the work done by the system is proportional to the heat consumed by the system. In a cyclic process in which the system does work on its surroundings, it is necessary that some heat be taken in by the system and some be put out, and the difference is the heat consumed by the system in the process. The constant of proportionality is universal and independent of the system and was measured by Joule in 1845 and 1847.

In any incremental process, the change in the internal energy is considered due to a combination of heat added to the system and work done by the system. Taking dU as an infinitesimal (differential) change in internal energy, one writes

$$dU = \delta Q - \delta W \tag{1}$$

whereδQ and δW are infinitesimal amounts of heat supplied to the system and work done by the system, respectively. Note that the minus sign in front of δW indicates that a positive amount of work done by the system leads to energy being lost from the system. (An alternate convention is to consider the work performed on the system by its surroundings. This leads to a change in sign of the work. This is the convention adopted by many modern textbooks of physical chemistry, such as those by Peter Atkins and Ira Levine, but many textbooks on physics define work as work done by the system.)When a system expands in a quasistatic process, the work done on the environment is the product of pressure (P) and volume (V) change, i.e. PdV, whereas the work done on the system is -PdV. The change in internal energy of the system is:

$$dU = \delta Q - PdV. \tag{2}$$

Work and heat are expressions of actual physical processes which add or subtract energy, while U is a mathematical abstraction that keeps account of the exchanges of energy that befall the system. Thus the term heat for δQ means that amount of energy added as the result of heating, rather than referring to a particular form of energy. Likewise, work energy for δW means "that amount of energy lost as the result of work". Internal energy is a property of the system whereas work done and heat supplied are not. A significant result of this distinction is that a given internal energy change dU can be achieved by, in principle, many combinations of heat and work.The internal energy of a system is not uniquely defined. It is defined only up to an arbitrary additive constant of integration, which can be adjusted to give arbitrary reference zero levels. This non-uniqueness is in keeping with the abstract mathematical nature of the internal energy.

IV. SECOND LAW OF THERMODYNAMICS

The *second law of thermodynamics* is an expression of the tendency that over time, differences in temperature, pressure, and chemical potential equilibrate in an isolated physical system. From the state of thermodynamic equilibrium, the law deduced the principle of the increase of entropy and explains the phenomenon of irreversibility in nature. The second law declares the impossibility of machines that generate usable energy from the abundant internal energy of nature by processes called *perpetual motion of the second kind*. The second law may be expressed in many specific ways, but the first formulation is credited to the German scientist Rudolf Clausius. The law is usually stated in physical terms of impossible processes. In classical thermodynamics, the second law is a basic *postulate* applicable to any system involving measurable heat transfer, while in statistical thermodynamics, the second law is a *consequence* of unitarity in quantum theory. In classical thermodynamics, the second law defines the concept of thermodynamic entropy, while in statistical mechanics entropy is defined from information theory, known as the Shannon entropy.

A. Description

The first law of thermodynamics provides the basic definition of thermodynamic energy, also called internal energy, associated with all thermodynamic systems, but unknown in mechanics, and states the rule of conservation of energy in nature.

However, the concept of energy in the first law does not account for the observation that natural processes have a preferred direction of progress. For example, spontaneously, heat always flows to regions of lower temperature, never to regions of higher temperature without external work being performed on the system. The first law is completely symmetrical with respect to the initial and final states of an evolving system. The key concept for the explanation of this phenomenon through the second law of thermodynamics is the definition of a new physical property, the entropy. A change in the entropy (S) of a system is the infinitesimal transfer of heat (Q) to a closed system driving a reversible process, divided by the equilibrium temperature (T) of the system.

$$dS = \frac{\delta Q}{T} \tag{3}$$

The entropy of an isolated system that is in equilibrium is constant and has reached its maximum value. Empirical temperature and its scale is usually defined on the principles of thermodynamics equilibrium by the zeroth law of thermodynamics. However, based on the entropy, the second law permits a definition of the absolute, thermodynamic temperature, which has its null point at absolute zero. The second law of thermodynamics may be expressed in many specific ways, the most prominent classical statements[3] being the original statement by Rudolph Clausius (1850), the formulation by Lord Kelvin (1851), and the definition in axiomatic thermodynamics by Constantin Carathéodory (1909). These statements cast the law in general physical terms citing the impossibility of certain processes. They have been shown to be equivalent [17].

B. Clausius Statement

German scientist Rudolf Clausius is credited with the first formulation of the second law, now known as the Clausius statement:

No process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature.

Spontaneously, heat cannot flow from cold regions to hot regions without external work being performed on the system, which is evident from ordinary experience of refrigeration, for example. In a refrigerator, heat flows from cold to hot, but only when forced by an external agent, a compressor.

C. Kelvin Statement

Lord Kelvin expressed the second law in another form. The Kelvin statement expresses it as follows:

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

This means it is impossible to extract energy by heat from a high-temperature energy source and then convert all of the energy into work. At least some of the energy must be passed on to heat a low-temperature energy sink. Thus, a heat engine with 100% efficiency is thermodynamically impossible. This also means that it is impossible to build solar panels that generate electricity solely from the infrared band of the electromagnetic spectrum without consideration of the temperature on the other side of the panel (as is the case with conventional solar panels that operate in the visible spectrum).Note that it is possible to convert heat completely into work, such as the isothermal expansion of ideal gas. However, such a process has an additional result. In the case of the isothermal expansion, the volume of the gas increases and never goes back without outside interference.

D. Principle of Carethedory

Constantin Carathéodory formulated thermodynamics on a purely mathematical axiomatic foundation. His statement of the second law is known as the Principle of Carathéodory, which may be formulated as follows:

In every neighborhood of any state S of an adiabatically isolated system there are states inaccessible from S.

With this formulation he described the concept of adiabatic accessibility for the first time and provided the foundation for a new subfield of classical thermodynamics, often called geometrical thermodynamics [17].

Equivalence of the statements Derive Kelvin Statement from Clausius Statement. Suppose there is an engine violating the Kelvin statement: i.e., one that drains heat and converts it completely into work in a cyclic fashion without any other result. Now pair it with a reversed Carnot engine as shown by the graph. The net and sole effect of this newly created engine consisting of the two engines mentioned is

$$\Delta Q = Q\left(\frac{1}{\eta} - 1\right) \tag{4}$$

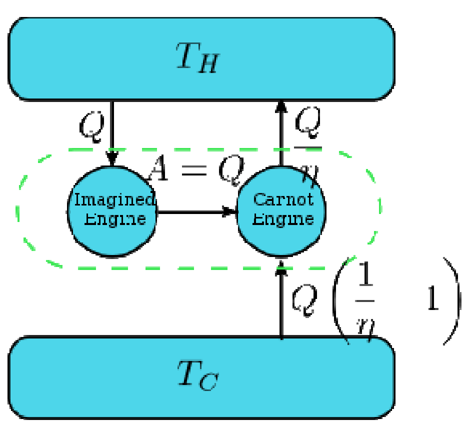

Fig. 1: Cooler reservoir to the hotter one, which violates the Clausius statement

transferring heat from the cooler reservoir to the hotter one (Fig. 1), which violates the Clausius statement. Thus the Clausius statement implies the Kelvin statement. We can prove in a similar manner that the Kelvin statement implies the Clausius statement, or, in a word, the two are equivalent.

V. INDUSTRIAL ECOLOGY

Industrial Ecology (IE) is the study of material and energy flows through industrial systems. The global industrial economy can be modeled as a network of industrial processes that extract resources from the Earth and transform those resources into commodities which can be bought and sold to meet the needs of humanity. Industrial ecology seeks to quantify the material flows and document the industrial processes that make modern society function [18]. Industrial ecologists are often concerned with the impacts that industrial activities have on the environment, with use of the planet's supply of natural resources, and with problems of waste disposal. Industrial ecology is a young but growing multidisciplinary field of research which combines aspects of engineering, economics, sociology, toxicology and the natural sciences. Industrial Ecology has been defined as a "systems-based, multidisciplinary discourse that seeks to understand emergent behavior of complex integrated human/natural systems". The field approaches issues of sustainability by examining problems from multiple perspectives, usually involving aspects of sociology, the environment, economy and technology. The name comes from the idea that we should use the analogy of natural systems as an aid in understanding how to design sustainable industrial systems. *Industrial Ecology* (IE) is the study of material and energy flows through industrial systems. The global industrial economy can be modeled as a network of industrial processes that extract resources from the Earth and transform those resources into commodities which can be bought and sold to meet the needs of humanity. Industrial ecology seeks to quantify the material flows and document the industrial processes that make modern society function. Industrial ecologists are often concerned with the impacts that industrial activities have on the environment, with use of the planet's supply of natural resources, and with problems of waste disposal. Industrial ecology is a young but growing multidisciplinary field of research which combines aspects of engineering, economics, sociology, toxicology and the natural sciences. Industrial Ecology has been defined as a "systems-based, multidisciplinary discourse that seeks to understand emergent behavior of complex integrated human/natural systems". The field approaches issues of sustainability by examining problems from multiple perspectives, usually involving aspects of sociology, the environment, economy and technology. The name comes from the idea that we should use the analogy of natural systems as an aid in understanding how to design sustainable industrial systems. Industrial ecology was popularized in 1989 in a *Scientific American* article by Robert Frosch and Nicholas E. Gallopoulos.

Frosch and Gallopoulos' vision was "why would not our industrial system behave like an ecosystem, where the wastes of a species may be resource to another species? Why would not the outputs of an industry be the inputs of another, thus reducing use of raw materials, pollution, and saving on waste treatment?" A notable example resides in a Danish industrial park in the city of Kalundborg. Here several linkages of byproducts and waste heat can be found between numerous entities such as a large power plant, an oil refinery, a pharmaceutical plant, a plasterboard factory, an enzyme manufacturer, a waste company and the city itself. The scientific field Industrial Ecology has grown quickly in recent years [19]. The Journal of Industrial Ecology (since 1997), the International Society for Industrial Ecology (since 2001), and the journal Progress in Industrial Ecology (since 2004) give Industrial Ecology a strong and dynamic position in the international scientific community. Industrial Ecology principles are also emerging in various policy realms such as the concept of the Circular Economy that is being promoted in China. Although the definition of the Circular Economy has yet to be formalized, generally the focus is on strategies such as creating a circular flow of materials, and cascading energy flows. An example of this would be using waste heat from one process to run another process that requires a lower temperature. The hope is that strategy such as this will create a more efficient economy with fewer pollutants and other unwanted by products [20].

VI. CONCULATION

In this paper about the important concept of thermodynamic as exergy, entropy, the first and second law of thermodynamic, industrial ecology and their application has been discussed. Industrial Ecology (IE) is the study of material and energy flows through industrial systems. The global industrial economy can be modeled as a network of industrial processes that extract resources from the Earth and transform those resources into commodities which can be bought and sold to meet the needs of humanity. Industrial ecology seeks to quantify the material flows and document the industrial processes that make modern society function.

REFERENCES

[1] T. Gundersen, An introduction to the concept of exergy and energy quality, Department of Energy and Process Engineering, Norwegian University of Science and Technology, Trondheim, Norway, Version 3, November 2009

[2] A. Bejan, G. Tsatsaronis, and M. Moran. *Thermal Design and Optimization*, Wiley, New York, 1996.

[3] M.J. Moran and E. Sciubba, “Exergy analysis: principles and practice”, *Journal of Engineering Gas Turbine Power*, Vol. 116, pp.285-302, 1994.

[4] M.A. Rose, Second-law analysis: Approaches and implications, *International Journal of Energy Research*, Vol. 23, pp. 415–29, 1999.

[5] M.A. Rosen, M.N. Le and I. Dincer ‘Thermodynamic assessment of an integrated system for cogeneration and district heating and cooling’, *International Journal of Exergy*, Vol. 1, pp.94–110, 2004.

[6] I. Dincer, The role of exergy in energy policy making, *Energy Policy*, Vol. 30, pp.137–149, 2004.

[7] Xi Ji. Chen, G.Q**.,** Chen, B. and Jiang, M.M, Exergy-based assessment for waste gas emissions from Chinese transportation', *Energy policy*, Vol. 37, pp. 2231-2240, 2009.
[8] A. Al-Ghandoor, E. Phelan, R. Villalobos and J.O. Jaber, 'Energy and exergy utilizations of the U.S. manufacturing sector', *Energy*, Vol. 35, pp. 3048-3065, 2010.
[9] J. Szargut and R. Petela, *Egzergia*, WNT, Warsaw 1965.
[10] J. Szargut and R. Petela, *Eksergi*ja, Energija, Moscow 1962.
[11] J. Szargut, D.R. Morris and F.R. Steward, *Exergy Analysis of Thermal, Chemical, and Metallurgical Processes* Hemisphere Publishing Corporation, New York 1988.
[12] R. Petela, Exergy of undiluted thermal radiation, *Solar Energy*, Vol. 74, pp. 469-488, 2003.
[13] R.Petela, Exergy analysis of the solar cylindrical-parabolic cooker, *Solar Energy,* Vol. 79, pp. 221-233, 2005.
[14] I, Dincer.and M.A. Rosen, *Exergy, Energy, Environment and Sustainable Development*, Elsevier, London, 2007.
[15] Y.A., Cengel, M.A. Boles, *Thermodynamics: An Engineering Approach*, 2nd Edition, McGraw-Hill, New York, 1994.
[16] J. Moran, H. Shapiro, *Fundamentals of engineering Thermodynamics*, 3nd Edition, McGraw-Hill, New York, 1994
[17] Internet, Wikipedia (www.wikipedia.com)
[18] B, Allenby, "The ontologies of industrial ecology". *Progress in Industrial Ecology,* Inderscience Enterprises Ltd., 2006.
[19] "The Kalundborg Centre for Industrial Symbiosis". http://www.symbiosis.dk. Retrieved 2007.
[20] ZBi, J, Yuan, Z, Y. Moriguichi,. "The Circular Economy: A New Development Strategy in China". *Journal of Industrial Ecology,* Vol. 10 (1-2), pp. 4–8.