THERMODYNAMIC ANALYSIS OF PROCESSES

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Summary

Thermodynamic analysis is one of the scientific tools of great importance for the study of nature consisting of countless and the most diversified processes of energy change. The analysis looks at these processes from the point of view of energy, entropy and exergy. In addition to traditional energy, entropy assessing the irreversibility of the process, a powerful exergy concept was used to draw conclusions that had not previously been achievable. The meaning of the exergy of any matter is that it determines for man the practical value of matter, measured by the ability to perform useful work. The methodology and specific objectives of the analysis are presented. The analysis introduces the concept of a considered system, precisely defined by the boundary of the system. The principle of mass conservation and thermodynamic laws have been applied to the systems under consideration. Possible forms of energy and exergy exchanged with the system are: kinetic, potential, chemical, physical, electrical, nuclear, work, heat, radiation. These components are taken into account in the equations

of entropy, energy and exergy. Sample formulas are presented to calculate typical components. Systems can be examined as constant or variable over time, in varying environments and with the input of gravity. An overall assessment of the system under consideration can be made on the basis of an analysis of the value of the components of the balance equations. Processes can be interpreted by their efficiency, defined in a way to bring out meaningful aspects. Carnot's efficiency assesses the maximum possibility of generating energy. The degree of perfection classifies energy and exergy components as either driving a process or as expected effects or as losses that may be irreversible or recoverable. Specific evaluation criteria have been applied for spontaneous processes, such as cooling and drying, during which the exergy is naturally annihilated. It was possible to provide only an overview of the thermodynamic analysis, as the analysis may cover a wide range of issues in a wide range of different fields, only a few of which are briefly mentioned in the conclusions. Considerations are mainly based on the disciplines of engineering thermodynamics and heat transfer, which the readers are advised to familiarize themselves with.

1. Importance of Thermodynamic Analysis

Thermodynamics is the science of energy and its transformations. Surrounding nature is insistently studied by many microscopic methods (e.g. microscopic observation or differential calculus) or macroscopic methods (considering phenomena or integral calculus). Processes in which any matter is involved are related to energy and occur according to the thermodynamic laws, which have been formulated based on observation of the nature. These laws cannot be mathematically proven, or derived, but their validity confirms the fact that never any process, occurring against these laws, has been noticed. Additionally, in the same way was formulated also the law of matter conservation. These all laws are used in thermodynamic analysis and its importance is that it can be used to study the most diverse processes, in which energy conversion occurs. A process can be simple or complex, consisting of multiple sub-processes. For example the analysis can be applied to the entire industrial sectors, the national power grid, industrial manufacturing, steel making, or chemical products, power plants, refineries, fuels combustion, steam boiler, car engine, plant growth, ecological and biological areas, concerning the human body, human cells, some say that even such a simple phenomenon, like sneezing, requires energy and causes an increase in entropy. Any physical and chemical as well as any macroscopic and microscopic processes can be subject to thermodynamic analysis. One has to be prepared, because sometimes, the perception and formulation of a process to analysis can be even a new discovery.

The thermodynamic analysis applies the First Laws of Thermodynamics, according to which the energy, defined as certain ability to do work, does not disappears, although can take other form, or dissipate. The Second Law of Thermodynamic introduces concept of entropy, as a certain thermodynamic function of state of any matter, and expresses the thermodynamic probability of the state of this matter. Entropy applied to the materials taking part in processes, allows to determine the process direction and to measure the process irreversibility. The loss of ability to work is the consequence of irreversibility and to better comprehend this effect, the thermodynamic function of matter, called exergy, was introduced and defined as a measure of ability to do work, like energy, but in the conditions of the natural human environment.

The thermodynamic analysis provides different views on the object under consideration. The views are in terms of the engineering quantity, probability and quality by respectively using of energy, entropy and exergy. Typical analysis is based on the material conservation equations that are respectively used for developing the energy balances, calculations of entropy values and for providing supplementary exergy balances. Such analysis allows to:
-   better understand any process,
-   facilitate design and control,
-   point at the needs for process improvement,
-   enable eventual optimization,
-   determine the degree of perfection of energy utilization in the process, or its particular parts,
-   compare the degree of perfection, and the related process parameters, to those in other similar processes,
-   compare of perfection and parameters to the currently achievable values in the most efficient systems,
-   establish the priorities for the required optimization attempts for the systems or its components. Such establishing can be carried out either based on the excessive energy consumptions or on the particularly low degree of perfection,
-   motivate the eventual change of technology.

In practice, there may be many systems under consideration, some of which are very complex. Complex systems usually deserve a fully extended analysis, but some simple problems can only be sufficiently investigated on the basis of energy analysis or exergy. It is very difficult to describe the details of thermodynamic analysis for each possible system. Therefore, only an outline of the overall methodology was discussed. The topic is very extensive and a better understanding of the issues discussed will be achieved by a reader who knows the basics of thermodynamics and heat transfer, because the ultimate goal of these two subjects is thermodynamic analysis of processes.

2. Considered System

A precise description and definition of the system under consideration is very important in order to obtain the correct results. Sometimes the situation is very complicated. The elements taken into account in the consideration should be clearly separated from the excluded elements. This explanation is effectively achieved by introducing an imaginary system boundary that tightly separates the system from the environment. The best way to do this is to draw a schematic of the contents of the system under consideration, clearly separated from the environment by a drawn line of the system boundary. This approach sometimes avoids many interpretive errors.

An effectively defined system can be a prerequisite for obtaining the desired results. Sometimes the problem can be effectively solved by using subsystems, also precisely defined. Re-determining the system often helps to obtain more valuable analysis results. Typically, the definition of a boundary for a system is obvious, but in some complex situations, how to define a system can be a new discovery.

The system boundary makes it easier to log events in the system. The mass of the substance can enter or leave the system, or accumulate in the system. The exchange of energy and exergy with the system is carried out in the same way, and for example the energy can be exchanged by:
- Streams of substances which may have physical, chemical or nuclear energy,
- Work, which is one way of transmitting energy,
- Heat, which is another way of transmitting energy,
- Electricity,
- Significant speed of the substance (kinetic energy),
- Interactions with the gravitational field (potential energy of the substance due to significant   altitude or buoyancy),
- Interactions with the electromagnetic radiation field (interpreted as a photon gas flux),
- Other force fields, such as surface tension (in a specific cases).

The energy components or exergy components of the system are the same, for example, the energy components can be:
- The internal energy of the molecules of the substance expressed by specific heat at constant volume,
- The kinetic energy of the substance,
- The potential energy of the substance,
- Other specific, such as surface tension.

Entropy is calculated for substances, heat and radiation.

The same system or subsystems must be used in the analysis of entropy equations and the conservation of mass, energy and exergy. Entropy calculations and balance equations can be developed for each formulated system or subsystem. Each equation allows you to calculate an unknown or can describe the relationship between variables.

Sometimes, to better understand the problem, you may apply a system boundary for an elementary part of the system. In this case, the equations of mass, energy, entropy and exergy must be used in differential form.

3. Mass Conservation Equations

Matter can be either a substance (material) which is a collection of elementary chemical particles, or a field matter that appears as the various field forces, e.g. gravity or electromagnetic radiation. Mass is the property of any matter and represents its inertia. Mass is used as a measure of the amount of substance by its weight in a gravitational field.

In physical processes the amount of particular molecules of substances does not change. However, due to chemical reactions in chemical processes unchanged is only the amount of particular chemical element. In nuclear processes unchanged remains the number of indivisible particles of matter. Therefore, based on the law of mass conservation, the conservation equations are applied respectively for the unchanging kinds of matter. However, in nuclear processes, the mass conservation law corresponds

to the energy conservation law as the consequence of the Einstein's formula determining the change of energy due to change of mass. The substance conservation equation does not need to include a radiation or any other form of matter except substance.

The mass (m_{in}) of all portions of balanced compound (in physical processes), or balanced chemical element (in chemical processes) entering the system, is equal to the mass ($\Delta m \ \Delta m$) of balanced species accumulated in the system and to the mass (m_{out}) of all portions of balanced species leaving the system:

$$m_{in} = \Delta m + m_{out} \ . \tag{1}$$

A particular form of substance conservation equation that can be written without any system boundary is the summarizing fractions ($f_i \ f_i$) of the each (i-th) component in the considered composite material:

$$m_{in} = \Delta m + m_{out} \ . \tag{2}$$

4. Energy Analysis

4.1. Internal Energy and Enthalpy

To determine the substance that exists at any given time, the state parameters of the substance, such as temperature and pressure, are used. For better organization of considerations, these state parameters are used to define additional various criteria, also describing the substance. Such criteria, called the state functions, are, for example, internal energy, enthalpy and later discussed entropy or exergy.

Internal energy is used for calculation of energy of substance when it always remains within the system boundary. This energy results from the microscopic motions, potential and structure of molecules. For example, internal energy (U) of ideal gas is calculated with use of specific heat (c_v) at constant volume:

$$U = m \, c_v T \ , \tag{3}$$

where (m) and (T) are the mass and absolute temperature of substance, (Burghardt, 1982).

Enthalpy is used to calculate the energy of a substance that passes through the system boundary, by entering or leaving the system. The enthalpy includes the transport work required to cross the border of the system. For example, in the case of a physical process, the enthalpy (H_{ph}) of the ideal gas is calculated using the specific heat (c_p) at constant pressure:

$$H_{ph} = m \, c_p T \ . \tag{4}$$

If specific substances, i.e. chemical compounds or chemical elements, are involved in chemical reactions in the system to be considered, the **chemical energy** of the substance should be taken into account. The chemical compound is a combination of some of the 118 existing chemical elements. Each chemical compound or chemical element has the ability to release heat during its disappearance in a chemical reaction. The heat released in such a reaction is the result of the thermal capacity of all reactants and is always the same for the same reaction. The values that determine the ability of the reacting substance to release heat can be assumed freely, but provided that the heat of the reaction between the substances in question is always the same. It is therefore convenient to adopt these values as zero for 118 freely selected reference substances. However, the value for each of the remaining substances must already be calculated on the basis of the thermal effect of the chemical reaction in which the substance reacts.

For example, the *enthalpy of formation method* assumes zero values for all chemical elements, and on this basis one can specify enthalpy of formation for any chemical compound. Such a reference level is not practical, however, because, for example, the value of a pure chemical element of a carbon is represented by a zero chemical value, while the product of combustion of such a carbon, practically useless CO_2, has a value of -394 MJ/kmol. Therefore the *devaluation enthalpy method* adopts zero reference values for 118 substances selected as the most useless and widely available in the environment. For example, the reference substance for C is CO_2 gas, for H is H_2O gas, and for O it is simply O_2 gas. It is worth noting that in a particular case, when the substance consists only of C, O, H, N and S, the devaluation enthalpy of such a substance is equal to its calorific value. Devaluation enthalpy for C is 394 MJ/kmol, while for CO_2 it is zero. The devaluation enthalpy method fairly interprets the real values of the substance, and by taking the reference substance in the same way as for exergy, it allows chemical energy to be compared with chemical exergy, (Szargut et al, 1988).

The enthalpy (H) of any substance crossing the system boundary, in the case of a chemical reaction in the system, shall be assumed to be the sum of the physical enthalpy (H_{ph}) of the substance and its chemical enthalpy (H_{ch}):

$$H = H_{ph} + H_{ch} \ . \tag{5}$$

The H_{ch} value is the product of the mass m of the substance and of its devaluation enthalpy (d^0)

$$H_{ch} = md^0 \ . \tag{6}$$

For the most important substances, the devaluation enthalpy d^0, referred to the mass unit, is available in the appropriate tables.

4.2. Energy Conservation Equations and its Components

The basis for formulating any conservation equation comes from the observation of nature where often something transforms into something with possible accumulation of something. Even a growing child lives this way. Now, for example, consider behavior of energy. The energy delivered (E_{in}) to a system goes to the increase of the system energy (ΔE_S) and the energy (E_{out}) leaving the system:

$$E_{in} = \Delta E_S + E_{out} \ .$$
(7)

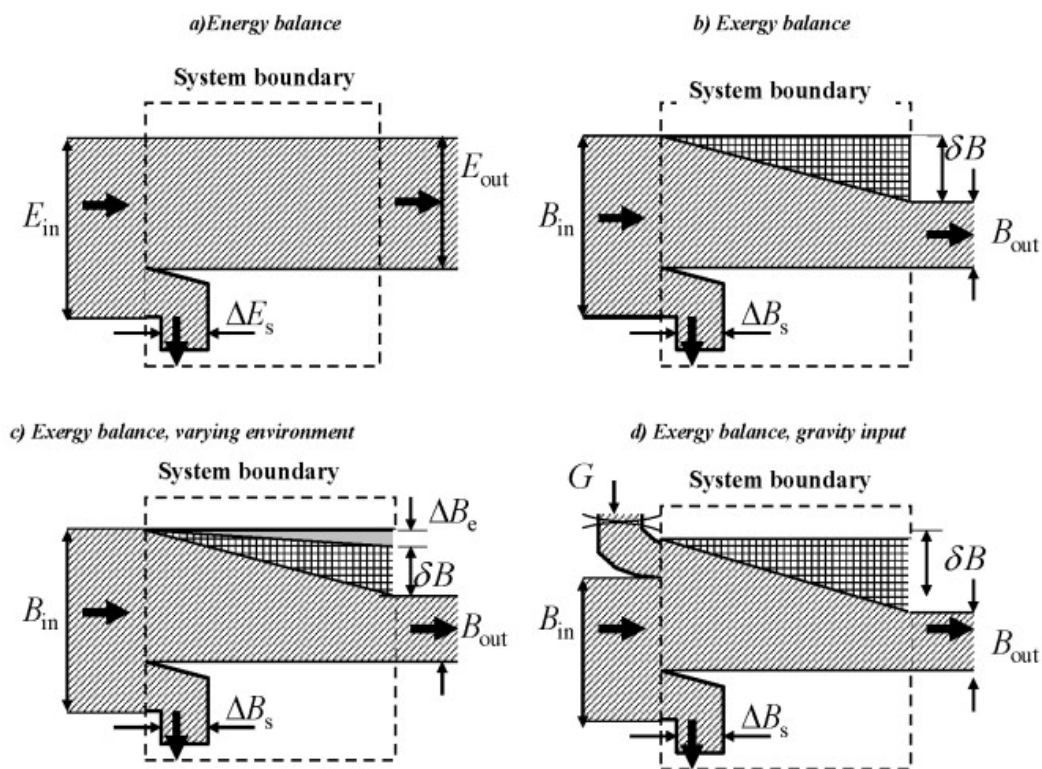The Eq. (7) can be illustrated using the Sankey diagram (Figure 1a).

Figure 1. Sankey diagrams for balances

The reference temperature for calculating energy is arbitrary, but it is recommended to adopt the environment temperature (T_0) for a better comparison with exergy, for which this temperature is determined by the definition of exergy.

The increase (ΔE_S) of system energy, changing from its initial to final state, does not depend on how this change is made and is the difference between the final ($E_{S,fin}$) and initial ($E_{S,inl}$) energy of the system:

$$\Delta E_S = E_{S,fin} - E_{S,inl} \ .$$
(8)

System energy can consist of macroscopic components ($E_{\text{macr},i}$) such as kinetic energy, surface tension energy, or potential energy due to gravity. Some of these components can be neglected if they are relatively small or remain constant, but atomization of liquid is an example of a process in which surface tension should be taken into account. The rest of the system energy is the internal energy (U_j) of the all system components:

$$E_{\text{S}} = \sum_i E_{\text{macr},i} + \sum_j U_j ,\qquad (9)$$

where (i) and (j) are successive indices of macro and micro components.

Energy (E_{in}) or (E_{out}) crossing the system boundary can occur in different ways. ***Electrical energy*** exchanged with the system is measured by means of a watt-meter. ***Mechanical work*** can only be exchanged with a piston rod or a rotary shaft. The energy of the exchanged ***streams of substance*** is determined by the enthalpy of substance. Also enthalpy is used for a diffusive exchange of substance. The ***kinetic energy*** of a substance should be taken into account if the substance in question has a velocity significant in relation to the system boundary. For the exchanged substance with a significant height above the reference level, the ***potential energy*** of the substance due to gravity field, should be taken into account. The system can exchange ***heat*** through conduction, convection and radiation. As a result of contact, heat can be exchanged by conduction or convection. Radiative heat exchange occurs without contact between heat exchanging bodies. The heat exchanged between objects is usually very specific in terms of geometrical configuration of the objects and the physical mechanism of the exchange process, and the corresponding calculations of the effects of heat exchange are discussed in many manuals (Holman, 2009).
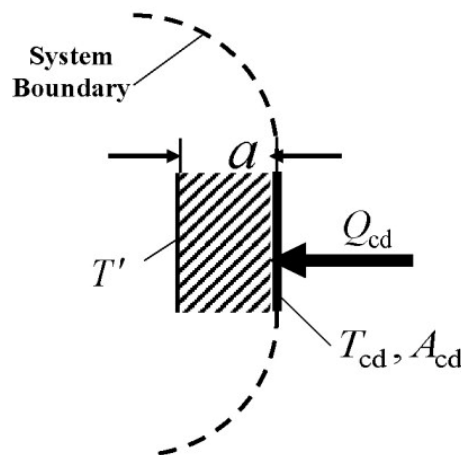

Figure 2. Absorbed heat

For example, over a period of time (Δt), heat (Q_{cd}) is conducted into the system through a layer of thickness (a), as shown in Figure 2. The surface area (A_{cd}) of the

layer has temperature (T_{cd}) and belongs to the system boundary. The second surface of the layer inside the system has temperature (T').   Calculated heat is:

$$Q_{cd} = A_{cd} k \frac{T_{cd} - T'}{a} \Delta t ,$$

(10)

where (k) is the thermal conductivity of the layer material.
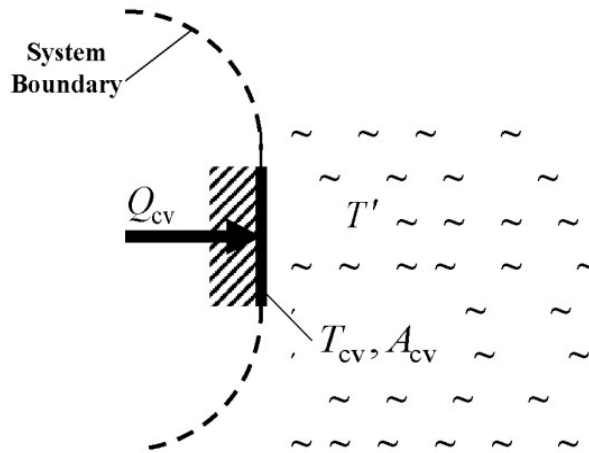

Figure 3. Released heat

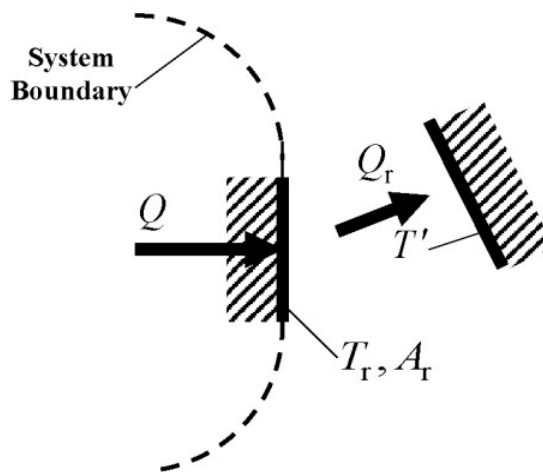Figure 4. Radiated heat

In other example, over a period of time (Δt), heat (Q_{cv}) is transferred (Figure 3) by convection from the surface of the (A_{cv}) area to the fluid at temperature (T'). This surface has a temperature (T_{cv}) and is part of the system boundary at temperature (T_{cv}). Calculated heat is:

$$Q_{cv} = A_{cv} \alpha \left(T_{cv} - T'\right) \Delta t ,$$

(11)

where (α) is the convective heat transfer coefficient.

In the next example, over a period of time (Δt), heat (Q_{cv}) is transferred by radiation (Figure 4) from the black surface (part of the system boundary) area (A_r) at temperature (T_r) to the other black surface at temperature (T'). The heat exchanged heat is:

$$Q_r = A_r \varphi_r \sigma \left(T_r^4 - T'^4 \right) \Delta t \ , \tag{12}$$

where (σ) is the Boltzmann constant for black radiation and (φ_r) is the view factor determining the solid angle at which the surface at temperature T' is seen from the surface at temperature T_r.

The real processes in the system occur with friction. Friction heat is partially either absorbed by the system and increases its energy or partially transferred from the system.

Equation (3) for the transient system may also be appropriately written for the steady system ($\Delta E_S = 0$), or for the system considered on a micro scale for which differential expressions are used.

In case of a moving system, the simplest equation of the energy balance can be obtained by assuming that the coordinates system determining the velocity and position moves along with the system boundary.

Equation (3) can be used in cases where one of the terms is zero, $E_{in} = 0, E_{out} = 0$, or $\Delta E_S = 0$. It is also possible if $E_{in} = 0$ and $E_{out} = 0$, which means that some processes can occur in the system with its energy unchanged, and this would be an example, when the energy approach, unlike the exergy approach, does not reveal the irreversibility of these processes.

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Bibliographical Sketch

Ryszard (Richard) Petela received his B. Sc. (1954), M. Sc. (1956), Ph. D. (1962), and Postdoctoral (1965) degrees from Silesian Technology University of Gliwice, Poland. He served as a professor of mechanical engineering at his alma mater from 1956–1984, where he researched and lectured courses in engineering thermodynamics, energy conversion processes, heat and mass transfer, combustion and fuel technology, supervised 73 Ph.D. and M.Sc. dissertations. He co-founded the Polish Scientific School of Exergy, and founded the Silesian Research School of Combustion. He served as the elected President of the Silesian University of Technology, and as a member of the Committees of the Polish Academy of Sciences. He was also the scientific consultant to the Ministry of Chemical Industry and Science on the subject of hybrid gasification process, and was a scientific and technical advisor for steam power stations, for the non-ferrous metallurgy industry, and for the steel industry. He also coordinated the government's "Energy" and "Coal" research programs. With his research team, he has implemented several technological ideas in steel industry furnaces. He was a member and a licensed expert of the Polish Mechanical Engineers and Technicians Association, the vice-president of the Silesian Section of the Polish Consultant Association, and a member of the scientific boards of four other organizations. He was scientific advisor at the North China Electric Power University at Beijing. He was a member of the American Chemical Society, the New York Academy of Science, and the American Association for the Advancement of Science. For many years he carried out editorial work for the University Research Archives, and was a member of the Editorial Advisory Board of the quarterly *Archivum Combustionis*, under the auspices of the Polish Academy of Science. He was an Associate Editor for the Journal of Solar Energy, and a member of the Editorial Board of the International Journal of Exergy. In 1963-1964 was the British Council Scholar visiting Universities of Sheffield, Leeds, Oxford, Cambridge and Imperial College in London. In 1974-1975 was the visiting researcher at University of Calgary. In 1984-1985 he was visiting Technical University in Vienna. As a former activist in the Solidarity movement in the scientific community, he left Poland in 1984 and immigrating to Canada. He was a visiting professor at the University of Calgary, he served as a research officer of the Alberta Research Council and he was the president of the consulting company Technology Scientific Ltd. His main research interests were focused on the engineering thermodynamics, especially exergy analysis and combustion, but also coal upgrading, waste heat recovery and other. He is the author or coauthor of about 160 refereed articles, authored several text books on combustion technology and book on heat transfer, coauthored pioneer monograph on "Exergy" in Polish and translated into Russian, and authored pioneer monograph on "Engineering Thermodynamics of Thermal Radiation", developing theory of radiation exergy, in English, translated into Chinese. He holds 12 patents. He was the principal investigator of 72 projects for both industrial and scientific institutions, and presented his research at over 100 national and international conferences.