Performance of a Thermoelectric Module Using the Thermodynamic Relationship Temperature-Entropy (T-S)

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Abstract

In this paper, the performance of a thermoelectric module is analysed using the thermodynamic diagram Temperature-Entropy. This diagram can be used as a graphical tool which allows for the analysis of thermoelectric processes, both reversible and non-reversible, in an elemental pair or thermoelectric elements.

A similarity is found between the *Seebeck* coefficient and entropy per unit of electrical charge. This allows for the use of the *Seebeck* coefficient and absolute temperature as coordinates in a representative Cartesian system. All processes, both reversible and non-reversible, in a pair of thermoelectric elements can be represented in the above mentioned system.

This analysis is completed with the identification of several graphic elements such as lines and areas, and their association to different equations and thermodynamic relationships of the thermoelectric module performance. This approach is very useful in the analysis of thermoelectric modules as it is performed from an engineering point of view in classical thermodynamics.

Seebeck coefficient and entropy

The *Seebeck* coefficient (σ) can be expressed according to equation 1. This is an expression from the *Onsager* relations [1] and [2] considering a bar of a thermal and electrical conductor material under the application of a potential electrical difference ($\boldsymbol{\varepsilon}$) and a difference of temperature (Δ**T**).

$$\sigma = \left.\frac{I_s}{I}\right)_{T=cte} = \left.\frac{I_Q \big/ T}{I}\right)_{T=cte} \tag{1}$$

Where:

$I_s = \dot{S} = \dfrac{dS}{dt}$ is the entropy per time unit which crosses a particular section.

$I = \dfrac{d\varsigma}{dt}$ is the electrical charge flow per time unit, that is, the electrical current through the same section.

Dividing the last two expressions, equation 1 can be transformed into equations 2 and 3.

$$\sigma = \frac{I_s}{I} = \frac{dS \big/ dt}{d\varsigma \big/ dt} = \frac{dS}{d\varsigma} \tag{2}$$

$$\sigma = \left.\frac{I_s}{I}\right)_{T=cte} = \left.\frac{dS}{d\varsigma}\right)_{T=cte} \tag{3}$$

If **T=cte,** the electrical charges do not receive heat due to the *Fourier* and *Joule* effect and then, the entropy of these charges is a property of the material where they are located at the temperature of the section analysed and it is called entropy transport parameter [1].

An important conclusion can be derived from equations 1 and 3 stating that the *Seebeck* coefficient of a particular material at a temperature can be interpreted as the entropy per electrical charge unit of that material and at that temperature.

Furthermore, the relationship between the *Seebeck* coefficient and the entropy can be verified by analysis of the *Thomson* effect in the material under study at a particular temperature [3].

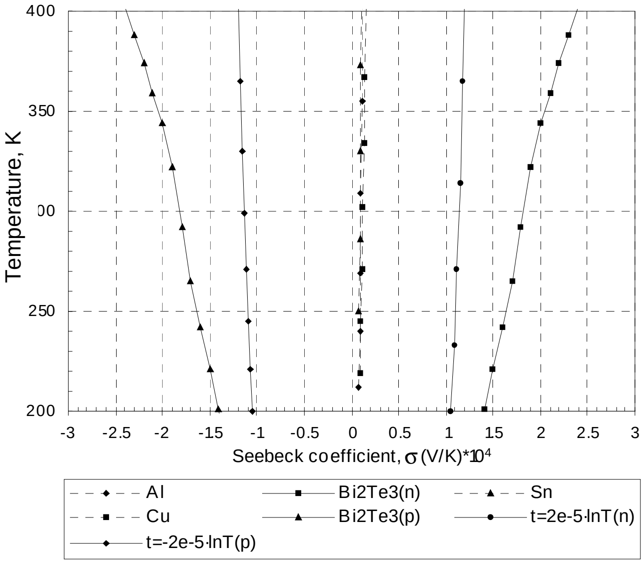

Figure 1. T-σ diagram for different materials.

Once it is accepted that the Seebeck coefficient can be interpreted as the entropy per electrical charge unit in a particular material, it is possible to use the relationship "Temperature-*Seebeck* coefficient" in order to analyse the thermoelectric process in a *Peltier* thermoelectric module. This will allow an analogy between the analysis of a thermodynamic process in the plane T-S and a thermoelectric process.

A diagram including the relationship **T-σ** for several materials is presented in figure 1. This graphic was constructed under the hypothesis of constant pressure, so the equation $f(T,\sigma)=0$ would be the thermoelectric state equation of each material.

After the previous results, the Seebeck coefficient can not be interpreted as the absolute entropy of the electrical charges. The reason for this is that the absolute entropy of any material can not be negative according to the Third Principle of Thermodynamics and as stated in figure 1, Bi_2Te_3 (n) has a negative Seebeck coefficient.

This fact is not contradictory, because the existence of negative values for the absolute *Seebeck* coefficient is associated to doped semiconductor materials where the *Seebeck* coefficient could be a consequence of electrical carriers with a different sign according to the doped process. So, these negative values for the *Seebeck* coefficient could be not absolute, but relative to the semiconductors type **p** or **n** analysed.

Qualitative description of the reversible effects of a thermoelectric pair in a T-σ diagram.

Figure 2 represents a typical scheme of a thermoelectric pair consisting of two materials A and B. This pair of elements is joined at two points through an electrical connection. A current of **I** A circulates through this electrical circuit. The two points of junction are at different temperatures **T1** and **T2**.

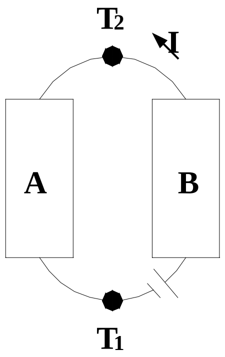

Figure 2. Scheme of a pair of thermoelements.

The objective of this section is the description of all the reversible effects in a pair of thermoelements by analogy with a thermodynamic cycle. Figure 2 will be used as reference in the following explanation.

The reversible thermoelectric effects, which would occur in the pair shown in figure 2, are plotted in figure 3. *Fourier* and *Joule* effects were not considered. The distinct processes appear due to the circulation of a certain amount of electrical charges per time unit (due to an electrical current of **I** A).

In figure 3, it can be observed that all the different processes occurring in a thermoelectric pair configure a closed cycle. In the case of a thermoelectric module for cooling (*Peltier* effect) the direction to follow the cycle would be **1-2-3-4-1**, the same as in a conventional inverse thermodynamic cycle for refrigeration, while the cycle has to be followed in the opposite direction **1-4-3-2-1** when a *Seebeck* thermoelectric module is analysed, the same as in a conventional direct thermodynamic cycle. Next the processes will be described.

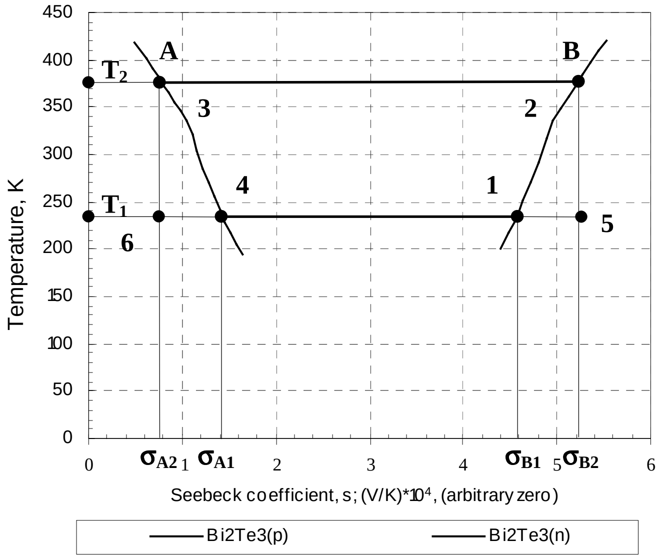

Figure 3. T-σ diagram of the reversible effects in a thermocouple.

Process **1-2** represents the different thermoelectric states of the distinct physical points along the thermoelement **B**. Points **1** and **2** of the diagram are the states at the ends of the thermoelement of which the temperatures are $\mathbf{T_1}$ and $\mathbf{T_2}$ respectively. Notice the one-dimensional and not topological sense of the representation used.

Process **2-3** represents the heat exchange between system and medium (environment) which occurs at the union between the two materials **A** and **B** at temperature $\mathbf{T_2}$. The intermediate states between **2** and **3** do not correspond with physic points in the thermoelements, therefore they are not thermoelectric equilibrium states.

Process **3-4** represents the different thermoelectric states of the distinct physical points along the thermoelement **A**. Points **3** and **4** of the diagram are the states at the ends of the thermoelement whose temperatures are $\mathbf{T_2}$ and $\mathbf{T_1}$ respectively.

Process **4-1** represents the heat exchange between the system and the medium which occurs at the union between the two materials **A** and **B** at temperature $\mathbf{T_1}$. The intermediate states between **4** and **1** do not correspond with physic points in the thermoelements, therefore they are not thermoelectric states of equilibrium.

The previous description of processes suggests that the characteristics of a thermoelectric plane **T-σ** are the same as those of a thermodynamic plane **T-s**. Next, these similarities will be enunciated.

- The areas comprised between the process lines and the abscissa axis represent the heat per unit of an electrical charge exchanged in the reversible processes.
- The area closed in the cycle represents the “net work” done by the unit of electrical charge. This work is positive, done by the system, when the cycle is followed clockwise and negative, done against the system, in the contrary direction.

- The “net work” performed is positive in the case of using a thermoelectric module for generating electricity (*Seebeck* effect), similar cycles are called “work cycles” in classical thermodynamics.
- The “net work” performed is negative when electrical energy is supplied to the system in order to absorb heat in the heat sink with less temperature and reject it in the heat sink with higher temperature (*Peltier* effect). This type of cycle is called the “inverse cycle” in classical thermodynamics.
- The graphical representation of the different processes in figure 3 is consistent with several states of the system, if they are considered to be one-dimensional, in such a way that the plotted states are the average of all the states which can exist in a cross section to the charge flow in the physic installation where the process is developed.
- It is assumed in the previous points that the flow of electrical charges is produced in stationary regimen. The properties of any point of the thermoelement do not change with time.
- The graphical representation of the processes in figure 3 is not topological. There is no proportionality between the distances from any point of a process to its end and the distance between the points corresponding to the physical system in which the process is developed.
- The thermoelements and specially their unions must be in contact with good thermal conductors to facilitate the heat exchange between system and medium.

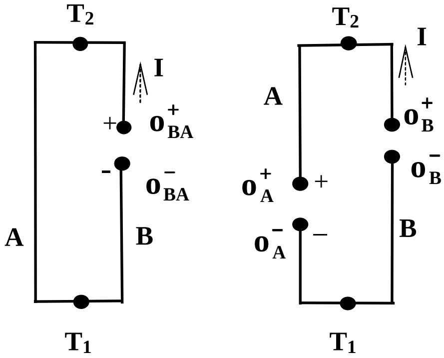

Figure 4. Interruption of the electrical circuit in one thermoelectric element (left side) and in both thermoelectric elements (right side) for connection of an electrical machine.

- It is necessary to interrupt the continuity of the electrical circuit through the thermoelements so that an electrical machine can be connected between the ends of the pair of the thermoelement in order to exchange work between the system and the medium. Both ends of the thermoelement will be at the same temperature. So, although the processes with exchange of work are represented in a continuous line in the T-σ diagram (see figure 3), in the physical configuration of the thermoelectric pair at least one of its thermoelements must be connected to the electric system which interacts with the thermoelectric pair. If the electrical circuit is only opened in a thermoelement, the work exchanged through its ends will be the “net work” of the cycle. This is represented in figure 4. If the electrical circuit is opened in both thermoelements, each of them exchanges the work associated with the process which occurs in that thermoelement, adding work in one of them and extracting it in the another one depending on the direction the cycle follows. This is represented in figure 4.

Mathematical analysis of the reversible effects of a thermoelectric pair in a T-σ diagram.

Once a qualitative description of all the reversible processes has been done, the mathematical relations which govern these processes will be formulated underlining the similarities between the **T-σ** and **T-s** diagrams.

All the processes to be presented will be opened systems in which the electrical charge per time unit, **I**, evolves and for that, the first principle of thermodynamics will be formulated using the following expression:

$$dq - dw = d\varepsilon \qquad (4)$$

All terms in equation 4 are expressed in units of energy per unit of electrical charge (**J/C**, or power per unit of electrical intensity, **W/A**). On the left side of the equation, the two terms represent respectively the heat and the work exchanged between the system and the medium, while the right term is the variation of the energy accumulated in the system due to the changes in its state variables. In this case, the only change is reduced to the variation in the electrical potential of the charges.

Next, all the processes which occur in a *Peltier* thermoelectric module are analysed in a separate way and then the complete cycle is studied. The numbers correspond to those used in figure 3. Only the reversible effects were considered.

Process **1-2**. This process is developed along the thermoelement **B**. Applying equation 4, the following expression will be obtained:

$$\int_1^2 dq - \int_1^2 dw = \int_1^2 d\varepsilon_B \qquad q_{12} - w_{12} = \varepsilon_{B2} - \varepsilon_{B1} \qquad (5)$$

If only reversible effects were being considered, the only heat exchanged would be the Thomson heat and the work performed would be associated with the *Seebeck* effect.

Thomson effect $\quad dq_T = Td\sigma_B \quad \Rightarrow \quad q_{12} = \int_1^2 Td\sigma_B$

Seebeck effect $\quad dw_S = \sigma_B dT \quad \Rightarrow \quad w_{12} = -\int_{T_1}^{T_2} \sigma_B dT$

In a T-σ diagram, the enclosed area between any curve T=*f*(σ), the abscissa axis and the ordinates corresponding to two points (**a** and **b**) of this curve is equivalent to $\int_a^b f(\sigma)d\sigma$. Then, as shown in figure 3, the area (**σ_{B1}-1-2-σ_{B2}**) limited by the line which defines the process **1-2** ($\sigma_B = f(T)$), the ordinates of these points **1** and **2** and abscissa axis (with the ordinate origin in the absolute zero, **T=0K**) represents the heat per unit of electrical charge absorbed by theThomson effect.

On the other hand, the enclosed area between any curve σ=*g*(T), the ordinate axis and the abscissas of two points (**a** and **b**) is equivalent to $\int_a^b g(T)dT$. Then, as shown in figure 3, the area (**T_1-1-2-T_2**) limited by the line which defines the process **1-2** ($\sigma_B = g(T)$), the abscissas of these points and the ordinate axis represents the work to be applied to the electrical intensity unit in order to move from state **1** to **2**, which is the *Seebeck* work.

The process **1-2** can not be adiabatic because it has to absorb the heat due to the Thomson effect which depends on the coefficient σ of the material. If this process would have to be externally reversible, the heat would have to be interchanged with infinite heat sources located along the thermoelement **B** and each of them would be at the same temperature as the section of the thermoelement which exchanges heat with it. The previous reasoning suggests that the thermoelement does not have to be isolated in its laterals. If this occurs, the *Thomson* heat would be transmitted by thermal conduction across the thermoelement producing effects that are not reversible and the temperature distribution would be different from the reversible case.

The process **1-2** would only be adiabatic if **σ_B = cte**, in this case, the *Thomson* heat would be null.

Process **2-3**. This process occurs at the physic union between the thermoelements **A** and **B** (one-dimensional model). The following expression is obtained applying equation 4 to the process:

$$q_{23} - w_{23} = \varepsilon_{A2} - \varepsilon_{B2} \tag{6}$$

Considering only reversible effects, the only heat exchanged in the process is the Peltier heat expressed by equation 7:

$$q_{23} = T_2(\sigma_{A2} - \sigma_{B2}) \tag{7}$$

The work performed is null, $w_{23} = 0$, because $dw_S = \sigma_B dT$ and **dT=0**, and then equation 6 can be rewritten as the following:

$$q_{23} = T_2(\sigma_{A2} - \sigma_{B2}) = \varepsilon_{A2} - \varepsilon_{B2} \tag{8}$$

Equation 8 is equivalent to the area **σ_{B2}-2-3-σ_{A2}** in figure 3. Then, this area represents the *Peltier* heat transferred from the system to the medium in the reversible process **2-3**.

Process **3-4**. This process is equivalent to process **1-2** but along the thermoelement A. Applying equation 4 and following the same procedure as in process 1-2, the following expression will be obtained

$$q_{34} - w_{34} = \int_3^4 T d\sigma_A + \int_{T_2}^{T_1} \sigma_A dT = \varepsilon_{A1} - \varepsilon_{A2} \tag{9}$$

In this case, the area **σ_{A2}-3-4-σ_{A1}** in figure 3 represents the *Thomson* heat per unit of electrical charge rejected by the system and the area **T_1-4-3-T_2** corresponds to the electrical work developed by the system in order to move the electrical intensity unit from state **3** to **4**. This process is not adiabatic if $\sigma_A \neq cte$.

Process **4-1**. This isothermal process is similar to process **2-3**, however it occurs in the physic union between both thermoelements **A** and **B** at temperature **T_1**. The following expression is obtained applying equation 4 to the process

$$q_{41} = T_1(\sigma_{B1} - \sigma_{A1}) = \varepsilon_{B1} - \varepsilon_{A1} \tag{10}$$

The expression in equation 10 is equivalent to the area **σ_{A1}-4-1-σ_{B1}** in figure 3. Then, this area represents the *Peltier* heat transferred from the medium to the system in the reversible process **4-1**.

The heat per unit of electrical charge supplied to the system in the cycle (**q_a**) would be:

$$q_a = \sum q_{ij}^{(+)} = q_{12} + q_{41} + q_{34} = \int_1^2 T d\sigma_B + T_1(\sigma_{B1} - \sigma_{A1}) + \int_3^4 T d\sigma_A$$

The heat per unit of electrical charge yielded by the system in the cycle (**q_c**) would be:

$$q_c = \sum q_{ij}^{(-)} = q_{23} = T_2(\sigma_{\mathbf{B}2} - \sigma_{A2})$$

The net heat per unit of electrical charge exchanged in the cycle (**q_n**) would be:

$$\begin{aligned} q_n &= q_a - q_c = q_{12} + q_{41} + q_{34} - q_{23} \\ &= \int_1^2 T d\sigma_B + \int_3^4 T d\sigma_A + T_1(\sigma_{B1} - \sigma_{A1}) - T_2(\sigma_{B2} - \sigma_{A2}) \\ &= area\,\sigma_{B1} 12 \sigma_{B2} + area\,\sigma_{\mathrm{A}1} 41 \sigma_{B1} - \\ &\quad - area\,\sigma_{B2} 23 \sigma_{A2} + area\,\sigma_{A2} 34 \sigma_{A1} \\ &= -area 12341 \end{aligned} \tag{11}$$

The net work (**w_n**) developed in the cycle would be:

$$\begin{aligned} w_n &= w_{12} + w_{34} = -\int_{T_1}^{T_2} \sigma_B dT + \int_{T_1}^{T_2} \sigma_A dT = \int_{T_1}^{T_2} (\sigma_A - \sigma_B) dT \\ &= -area\,\mathrm{T}_1 12 T_2 + area\,T_2 34 T_1 = -area 12341 \end{aligned} \tag{12}$$

It is obvious that the cycle verifies $q_n = w_n$ and then:

$$\int_{T_1}^{T_2} (\sigma_A - \sigma_B) dT = \int_1^2 T d\sigma_B - \int_4^3 T d\sigma_A + T_1(\sigma_{B1} - \sigma_{A1}) - T_2(\sigma_{B2} - \sigma_{A2})$$

Being **T** and **σ** state variables, the following relation can be written:

$$T_1(\sigma_{B1} - \sigma_{A1}) - T_2(\sigma_{B2} - \sigma_{A2}) = -\int_1^2 d[T(\sigma_B - \sigma_A)] \tag{13}$$

replacing and grouping terms in the equation above:

$$d(T\sigma_A) - T d\sigma_A - \sigma_A dT = d(T\sigma_B) - T d\sigma_B - \sigma_B dT = 0 \tag{14}$$

Knowing that $T\sigma = q_P$, *Peltier* heat, $T d\sigma = dq_T$, *Thomson* heat and $\sigma dT = d\varepsilon_S$, *Seebeck* work. The following equation is verified in a thermoelement:

$$dq_P = dq_T + d\varepsilon_S \tag{15}$$

The analysis of the electrical potentials can be started knowing that their addition has to be null $\sum_{cycle} \varepsilon = 0$, and:

$$\begin{aligned} \varepsilon_{B2} - \varepsilon_{B1} &= -\left[T_2(\sigma_{A2} - \sigma_{B2}) + \int_3^4 T d\sigma_A + \int_{T_2}^{T_1} \sigma_A dT + T_1(\sigma_{B1} - \sigma_{A1}) \right] \\ &= \int_1^2 T d\sigma_B + \int_{T_1}^{T_2} \sigma_B dT \end{aligned} \tag{16}$$

$$\begin{aligned} \varepsilon_{A2} - \varepsilon_{A1} &= T_2(\sigma_{A2} - \sigma_{B2}) + \int_1^2 T d\sigma_B + \int_{T_1}^{T_2} \sigma_B dT + T_1(\sigma_{B1} - \sigma_{A1}) \\ &= \int_3^4 T d\sigma_A + \int_{T_2}^{T_1} \sigma_A dT \end{aligned} \tag{17}$$

However these two last equations 16 and 17 do not express the difference of electrical potential which would exist at the ends of the connections to the hypothetical electric machines which would exchange work with the system, points $\mathbf{0_A}$ y $\mathbf{0_B}$ in figure 4. The electrical potential at these points can be expressed as follows:

$$\varepsilon_{o_B^+} = \varepsilon_{B2} - \int_0^2 Td\sigma_B \qquad \varepsilon_{0_A^+} = \varepsilon_{A2} + \int_3^0 Td\sigma_A$$

$$\varepsilon_{0_B^-} = \varepsilon_{B1} + \int_1^0 Td\sigma_B \qquad \varepsilon_{0_A^-} = \varepsilon_{A1} - \int_0^4 Td\sigma_A$$

Making the differences of the last expressions:

$$\varepsilon_{o_B^+} - \varepsilon_{0_B^-} = \varepsilon_{B2} - \varepsilon_{B1} - \int_1^2 Td\sigma_B = \int_{T_1}^{T_2} \sigma_B dT \qquad (18)$$

$$\varepsilon_{o_A^+} - \varepsilon_{0_A^-} = \varepsilon_{A2} - \varepsilon_{A1} + \int_3^4 Td\sigma_A = -\int_{T_2}^{T_1} \sigma_A dT \qquad (19)$$

If only one thermoelement is interrupted to exchange work between the system and the medium, the difference of electrical potential can be expressed as:

$$\varepsilon_{0BA} = \left(\varepsilon_{o_B^+} - \varepsilon_{0_B^-}\right) - \left(\varepsilon_{o_A^+} - \varepsilon_{0_A^-}\right) = \int_{T_1}^{T_2} (\sigma_B - \sigma_A) dT \qquad (20)$$

Obviously:

$$\varepsilon_{o_B^+} - \varepsilon_{0_B^-} = w_{12} \qquad \varepsilon_{o_A^+} - \varepsilon_{0_A^-} = w_{21} \qquad \varepsilon_{0BA} = w_n$$

The **cooling efficiency** of the inverse cycle can be calculated dividing the heat absorbed in the cycle by the "net work" supplied to it. This is expressed in equation 21.

$$\varepsilon_f = \frac{\dot{Q}_a}{\dot{W}_n} = \frac{q_a}{-(w_n)} = \frac{\int_1^2 Td\sigma_B + \int_3^4 Td\sigma_A + T_1(\sigma_{B1} - \sigma_{A1})}{\int_{T_1}^{T_2} (\sigma_B - \sigma_A) dT} \qquad (21)$$

The **coefficient of performance** (**COP**) of the same inverse cycle is the quotient between the heat rejected by the cycle and the "net work" supplied to it. This is equation 22.

$$cop = \frac{\dot{Q}_c}{\dot{W}_n} = \frac{q_c}{-(w_n)} = \frac{T_2(\sigma_{B2} - \sigma_{A2})}{\int_{T_1}^{T_2} (\sigma_B - \sigma_A) dT} \qquad (22)$$

If the cycle was analysed as a work cycle, its thermodinamic quality (also the thermoelectric one) would be measured with the thermal performance according to equation 23.

$$\eta_t = \frac{\dot{W}_n}{\dot{Q}_a} = \frac{w_n}{q_a} = \frac{\int_{T_1}^{T_2} (\sigma_B - \sigma_A) dT}{T_2(\sigma_{B2} - \sigma_{A2})} \qquad (23)$$

If in equations 21 to 23, the Seebeck coefficients of both thermoelements ($\boldsymbol{\sigma_A}$ and $\boldsymbol{\sigma_B}$) were independent from the temperature, the cooling efficiency, the COP and the thermal performance would be the values of a *Carnot* cycle ($\boldsymbol{\eta_{tC}}$, $\boldsymbol{\varepsilon_{fC}}$ and COP_C) working between the same temperatures. According to this, the main parameters mentioned would have the following expressions:

$$\varepsilon_f = \varepsilon_{fC} = \frac{T_1}{T_2 - T_1} \quad cop = cop_C = \frac{T_2}{T_2 - T_1} \quad \eta_t = \eta_{tC} = \frac{T_2 - T_1}{T_2}$$

Notice that because the material Seebeck coefficients are constants with the temperature, the Thomson heat would be null and the thermoelectric cycle will consist of two isothermal processes and two adiabatic ones alternated. This is the typical *Carnot* cycle in the classical thermodynamic processes.

In a real case, the Seebeck coefficients are not independent from the temperature, and the Thomson heat would appear in the pair of thermoelements. Although this effect is reversible, the thermal efficiency of the cycle (also reversible) would be less than or equal to the efficiency of the Carnot cycle working between the same temperatures. The reason, as in classic thermodynamics, is based on the fact that the heat exchanged by the *Thomson* effect comes from heat sources whose temperatures are lower or are transferred to sinks whose temperatures are higher than the temperatures of the isothermal processes in the cycle (in figure 3 cases **2-3** and **4-1**. Next, this will be verified in mathematical terms.

Taking into account figure 3, the expression of the thermal performance in equation 23 can be rewritten as:

$$\eta_t = \frac{w_n}{q_a} = \frac{area14321}{area\sigma_{A2}32\sigma_{B2}} \qquad (24)$$

The thermal efficiency of a Carnot cycle working between the same temperatures would be:

$$\eta_{tc} = \frac{w_{nc}}{q_{ac}} = \frac{area14321 + area512 + area463}{area\sigma_{A2}32\sigma_{B2}} \qquad (25)$$

Equations 24 and 25 demonstrate that $\boldsymbol{\eta_t \le \eta_{tC}}$.

Using the same method it can be verified that the cooling efficiency and the coefficient of performance in an inverse cycle have as upper limits the values corresponding to a Carnot cycle working between the same higher temperatures: $\boldsymbol{\varepsilon_f \le \varepsilon_{fC}}$ and $\mathbf{cop \le cop_C}$.

It is possible to achieve $\eta_{tc} \ge \eta_t$, $\varepsilon_f = \varepsilon_{fC}$, $cop = cop_C$ in a reversible thermoelectric cycle, whenever the values of **area 512** and **area 463** in figure 3 were the same but with different signs. This would occur if the lines which represent processes **1-2** and **3-4** in figure 3 were parallel, although not necessarily straight lines. That is, functions $\mathbf{T}=\boldsymbol{g}(\boldsymbol{\sigma_A})$ and $\mathbf{T}=\boldsymbol{g}(\boldsymbol{\sigma_B})$ can only differ in an additive constant, as shown in equation 26 obtained from equations 23 and 13.

$$\eta_t = 1 - \frac{T_1(\sigma_{B1} - \sigma_{A1})}{T_2(\sigma_{B2} - \sigma_{A2})} - \frac{\int_1^2 Td\sigma_B + \int_3^4 Td\sigma_A}{T_2(\sigma_{B2} - \sigma_{A2})} \qquad (26)$$

The temperature distribution inside the thermoelements of a pair of thermoelements is not lineal, so the $\mathbf{T}$-$\boldsymbol{\sigma}$ diagram for the reversible processes can adopt strange shapes but the $\mathbf{T}$-$\boldsymbol{\sigma}$ diagram continues being useful in order to represent the cycle and all the conclusions, specially the similarity between the **T-σ** and **T-s** planes, are valid.

The analysis performed in this paper has only taken into account the reversible effects (Peltier, Thomson and Seebeck) in a pair of thermoelectric elements. This analysis can be extended to consider non-reversible effects (Fourier and Joule) in a similar way. A study of non-reversible effects has also been developed by the authors, but the inclusion of this analysis would surpass the limits of this paper.

Conclusions

This paper has presented an engineering perspective of the processes occurring in a pair of thermoelectric elements. An analogy has been presented between a classical thermodynamic cycle, like a Carnot cycle, and the typical cycle of work performed by a pair of thermoelectric elements. The analogy has been based on the use of the thermodynamic diagram Temperature-Entropy. This diagram can be used as a graphical tool which allows for the analysis of thermoelectric processes, both reversible (*Peltier*, *Seebeck* and *Thomson*) and non-reversible (*Joule* and *Fourier*), in a pair of thermoelectric elements.

The use of the Temperature-Entropy diagram was selected because a similarity was found between the *Seebeck* coefficient and entropy per unit of electrical charge. This allowed for the use of the *Seebeck* coefficient and absolute temperature as coordinates in a representative Cartesian system. All processes, both reversible and non-reversible, in a thermoelectric element can be represented in the above mentioned system.

The paper describes the mentioned analogy using only reversible effects, however the authors have also extended this analysis to the non-reversible ones.

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