

A non-equilibrium phenomenological (two-points) theory of mass and heat transfer. Forces, system-source interactions and thermodynamic cycle applications

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Abstract

Classic heat and mass transfer assessment bases on a “single-point” (equilibrium point) theory (SPT), where the departure from the equilibrium point proportionally drives the interaction. This paper continues author’s past works [M.D. Staicovici, *Internat. J. Heat Mass Transfer* 43 (22) (2000) 4153–4173, 4175–4188; *Internat. J. Refrigeration* 23 (2) (2000) 153–167] with a non-equilibrium phenomenological theory of mass and heat transfer, characterized as a “two-points” theory (TPT). The notions of coupled, non-coupled and mixed transfer and the theory two points (equilibrium and ideal) for a system—source type interaction are introduced. Natural forces governing the coupled and non-coupled transfer are given for physical/chemical interactions. The paper shows mixed transfer phenomenological coefficients and proves three theory basic theorems. According to TPT, the non-coupled mass and heat transfer is proportional to the departure from the equilibrium point, but the mixed transfer, unlike SPT, is maximized when equilibrium point approaches the ideal point. TPT is applied to the cyclic mass and heat transfer analysis, using mass conservation law, first principle of thermodynamics and the natural force conservation property, what proves to be similar to Clausius integral, but having the advantage of practical utility. TPT is applied to a mixed transfer cycle of heat pipe type and to a comparative TPT/CAN study concerning the maximum power output of the Carnot irreversible cycle. In case of the heat pipe, for the first time a non-empirical explanation concerning its high heat transfer is given, identifying heat pipe working with the mixed transfer maximization conditions. Concerning the finite-time thermodynamics application, theories are essentially concordant to hope to be coupled in future for a more realistic cycle calculation. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

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1. Introduction

In the classic theory, the heat and mass transfer are evaluated in conjuncture with an equilibrium state, where the equilibrium point, thought in a dynamical sense, plays a crucial role. More often than not, same meaning is given to this point when interactions are taking place, e.g., with a phase change in an isolated system reaching equilibrium, or they occur in an open system in the presence of a source (infinite reservoir) and finish attaining equilibrium with that. Mathematically, an equilibrium point (marked by the index “e”) is expressed by equations of the following type

$$\begin{aligned} T_l &= T_g = T_e \\ p_l &= p_g = p_e \\ \mu_{1(2),l} &= \mu_{1(2),g} \end{aligned} \quad (1)$$

In Eq. (1), for the sake of clarity, we chose the particular case of a bi-phase gas/liquid and bi-component system. According to the classic assessment, heat and mass transfer are proportional to the system departure from the equilibrium point, what plays the role of a driving force. When this departure is null, heat and mass currents become zero. As a corollary, classic heat and mass transfer assessment bases on a “single-point” (equilibrium point) theory (SPT).

In previous papers [1,2], a good part of a non-equilibrium phenomenological theory of the mass and heat transfer (NEPhTMHT) was presented. This paper will set forth new theoretical and practical aspects of this theory. In the frame of NEPhTMHT, the mass currents are considered

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Nomenclature

| | |
|--------------------|---------------------------------------------------------------------------------------------------|
| A | species of reactant, reduced excess heat |
| c_p | specific heat at constant pressure $\text{kJ}\cdot\text{kmol}^{-1}\cdot\text{K}^{-1}$ |
| C | heat capacity $\text{kJ}\cdot\text{kg}^{-1}$ |
| d | reversibility flaw, Eq. (74) $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ |
| e | thermodynamic function, Eq. (16) $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ |
| f | figure of merit, Eq. (24) |
| h | specific enthalpy $\text{kJ}\cdot\text{kg}^{-1}$ |
| i | current number |
| j | interaction mass current $\text{mol}\cdot\text{s}^{-1}$, $\text{kg}\cdot\text{s}^{-1}$ |
| L | phenomenological coefficient $\text{kg}\cdot\text{Ks}\cdot\text{m}^{-2}$ |
| $\max(a, b)$ | maximum value amongst a and b |
| $\min(a, b)$ | minimum value amongst a and b |
| n | number of species or moles of a specie involved in a chemical reaction |
| p | partial pressure kPa, bar, ata |
| \dot{q} | heat flux $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ |
| r | ratios, Eq. (32), (35), (36) |
| s | specific entropy $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ |
| S | area m^2 |
| \dot{S} | source of entropy $\text{W}\cdot\text{K}^{-1}$ |
| T, t | temperature K |
| v | specific volume $\text{m}^3\cdot\text{kg}^{-1}$ |
| \dot{V} | temporal derivative of the total volume. $\text{m}^3\cdot\text{s}^{-1}$ |
| \dot{w}, \dot{W} | power $\text{W}\cdot\text{kg}^{-1}$, W |
| x | liquid mass fraction $\text{kg}\cdot\text{kg}^{-1}$ |
| X | natural thermodynamic force $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ |
| y | gas phase mass fraction $\text{kg}\cdot\text{kg}^{-1}$ |
| z | coordinate in the natural force definition domain |

Greek symbols

| | |
|-----------------|-----------------------------------------|
| ν | stoichiometric coefficient |
| $\dot{\Lambda}$ | exergy destruction velocity W |

| | |
|---------------|-------------------------------------------------------------------------------------------|
| ρ | density $\text{kg}\cdot\text{m}^{-3}$ |
| ε | finite value |
| α | global heat exchange coefficient $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ |
| μ | chemical potential $\text{kJ}\cdot\text{kg}^{-1}$ |

Subscripts

| | |
|--------------|---------------------------|
| c | condensation |
| classic | classic |
| ch | chemical |
| cpl | coupled |
| d | direct |
| ep | equilibrium point |
| f | fluid |
| g | gas |
| h | enthalpic |
| i | mass, indirect |
| mixed | mixed |
| ip | ideal point |
| l | liquid |
| m | melting |
| ncpl | non-coupled |
| p | constant pressure, pure |
| phenom | phenomenological |
| q | heat |
| r | reduced, reversible |
| s | source, sink, solid |
| T | constant temperature |
| v | constant volume, vapor |
| w | wall, warm, power |
| 0 | ambient |
| 1, . . . , 4 | points in diagram, Fig. 9 |
| ' | before interaction |
| " | after interaction |

the coupling currents and that of heat the coupled ones, therefore, when writing about the coupled processes at hand, we shall use the expression mass and heat transfer, rather than heat and mass transfer. As it will be further shown, unlike classic point of view, the NEPhTMHT is a “two-points” theory (TPT) (preferred abbreviation next). Accordingly, forces governing the mass and heat transfer will have different properties as compared to the classic driving forces, depending on the type of point involved in interaction. Finally, a few words for a better understanding of the TPT role: while the two theories, classic and TPT, are not contradictory, but can reciprocally complete, the latter is capable to explain processes that are difficult to be explained by the classic theory of heat and mass transfer, e.g., the problem of the ammonia bubble absorption [1,2], or the heat transfer mechanism in heat pipes, outlined in this paper.

2. Natural forces of the coupled and non-coupled mass and heat transfer

First we shall give a detailed explanation of the physical system, main principle and nomenclature of the TPT.

Basic hypothesis. The interactions at hand are considered to take place in a global system what has as constitutive parts one, two, or more systems and sources (infinite reservoirs). The systems can be mono-, bi-, or poly-component and can behave as isolated, adiabatic, closed, or open, when exchange among them and/or with sources mass, heat and mechanical work. The internal mechanical work annuls reciprocally among systems. Sources being of constant parameters, only systems evolution is searched. This theory is based upon the hypothesis according to which the total energy of the systems is considerably equal to their internal energy, that is their macroscopic kinetic energy, and the

external fields of any nature that act upon them, as well as their internal tensions are negligible (simple global system at rest). Under the circumstances, the heat exchanged by the global system among its various constitutive parts is based upon the exchange of total enthalpy.

Coupled/non-coupled mass and heat transfer. A coupled mass and heat transfer is a process characterized by:

- (a) the change of the phase (nature) of reacting systems;
- (b) the presence of a reaction (latent) heat; and
- (c) mass and heat currents that influence each other.

On the contrary, a non-coupled transfer does not involve reaction heat, and systems do not modify their number and initial phase (nature) during interaction.

Mixed transfer of mass and heat. The transfer between systems and sources, simultaneously taking place by coupled and non-coupled mass and heat currents, will be referred to hereinafter as *mixed transfer*.

Interaction type. In the general case, n' constitutive parts A'_i , $i = 1, \dots, n'$, of the global system interact among them by coupled and/or non-coupled mass and heat transfer, giving rise to n'' constitutive parts A''_i , $i = 1, \dots, n''$. Additionally, only interactions through an intermediary system between two or more sources have sense.

Natural forces. Thermodynamic non-equilibrium (natural) forces govern the coupled/non-coupled mass and heat transfer. They differ only formally from the classic thermodynamic ones (driving forces), here called equilibrium (ideal) forces [1]: natural forces describe the evolution of interacting systems without being known whether they reach equilibrium (this depends on the external conditions of interaction), whilst the ideal forces assume a priori that equilibrium already exists. The natural forces are vector dimensions, that is two mass and heat transfer processes serially connected, occurring between states A and B, and B and C, respectively, have same resulting natural force $(-\vec{X})_{AB} + (-\vec{X})_{BC}$ as that of the mass and heat transfer process taking place from state A directly to state C, $(-\vec{X})_{AC}$, or

$$(-\vec{X})_{AB} + (-\vec{X})_{BC} = (-\vec{X})_{AC} \quad (2)$$

Same vector dimension exhibit also mass and heat currents, proportional to the natural forces. In this paper the transfer is deemed to be axial and the forces to be more often than not scalar dimensions, without losing any useful information.

Basic points of interactions. This paper makes distinction between two kinds of points towards what systems could “evolve”. These points are defined by the state parameters (p, T, x, y, \dots) of the interacting constitutive parts. If such parameters define a source of constant parameters

(p, T, x, y, \dots) , then the respective point will be called *equilibrium (absolute) point*. Such point will be marked in this paper with index “ep”. The terms “equilibrium” and “absolute” are understood herein in the static sense, what does not depend on the searched system and does not alter unless the parameters of the source alter. Natural forces are defined in an equilibrium point, where take the value zero. As specified in [1] and as it is going to be further shown, the points of a second type are the *ideal (relative) points*. Such points will be marked in this paper with index “ip”. A point in this category is found in the interactions with coupled transfer. Depending on their nature, systems can have different coupled transfers (e.g., condensation (absorption), vaporization (generation), solidification, melting, sublimation, de-sublimation). For this reason, the ideal points will be called *ideal points of condensation, vaporization, etc.* The ideal point is an equilibrium point in the classic dynamic (statistical) sense [3], where the static equilibrium cannot be reached, for which reason it has been called “ideal”. The ideal point is defined by equations similar to those given in Eq. (1). A natural force is not defined in an ideal point [1]. Depending on the interacting system, the ideal point has also been called “relative”, in order to differentiate it even further from the absolute equilibrium point. Isolated systems with coupled transfer evolve towards an ideal point under the action of natural forces what comply with the postulate, lemma and corollary in [1]. In a mixed transfer process, ideal points also intervene, but their aspect is influenced by the interaction with the source. For this reason, in such points the natural force complies only partially with the lemma of [1], in the sense that the signs of the forces adjacent to the point are different, but their absolute value differs.

Entropy source, currents, natural forces and phenomenological coefficients. The stationary mass and heat transfer is studied in the non-equilibrium thermodynamics by means of the entropy source, given by [4]

$$\dot{S} = -\frac{\dot{A}}{T_0} = -\left(\sum j's' + \sum j''s''\right)_{\text{mass}} - \left(\sum \frac{j'_q}{T'} + \sum \frac{j''_q}{T''}\right)_{\text{heat}} \quad (3)$$

where j and j_q are mass and heat currents, respectively, marked by prime (') and second (''), before and, respectively, after the interaction. The summation in Eq. (3) is done over all systems of the global system. Here sources were not included simply because the corresponding terms in the entropy source equation, which shows their contribution to the global increase of entropy, are annulled. Eq. (1) can be also written as follows:

$$\dot{S} = j'_1(-X) \quad (4)$$

where j'_1 is one of the coupling mass currents (herein chosen the first), and $(-X)$ is the natural force. In its turn, the mass current is proportional to the force $(-X)$ and to a

phenomenological coefficient, L_1 , according to the equation below

$$j'_1 = L_1(-X) \quad (5)$$

In its general form, according to the working hypothesis of the theory the force has the expression

$$(-X) = -\left(\sum j'_{i,r} s'_i + \sum j''_{k,r} s''_k\right) - \left(\sum j'_{i,r} \frac{h'_i}{T'} + \sum j''_{k,r} \frac{h''_k + j_q}{T''}\right) \quad (6)$$

where $j'_{i,r} = j'_i/j'_1$ and $j''_{k,r} = j''_k/j''_1$, $i = 1, \dots, n'$, $k = 1, \dots, n''$, j_q is the reaction, latent or sensible heat resulting from interactions, and h' and h'' are the specific enthalpies of the interacting constitutive parts before and after interaction, respectively.

Natural forces of the coupled transfer. The coupled transfer is dealt with in detail in [1,2]. It occurs in the case of physical or chemical interactions.

1. Mono-, bi- and particularly poly-component systems with physical interaction in non-ideal mixture.

$$(-X)_{\text{cpl}} = -\left[X_i + h_g \left(\frac{1}{T_g} - \frac{1}{T_i}\right) + \frac{Ah_1}{T_i[1 + AL_{\text{cpl}}(-X_{\text{cpl}})]}\right] \times \left[1 + \frac{A(h_g - h_1)}{T_i[1 + AL_{\text{cpl}}(-X_{\text{cpl}})]}\right]^{-1} \quad (7)$$

where

$$X_i = (s_g - s_l) - (y - x) \left(\frac{\partial s_l}{\partial x}\right)_{p,T} \quad (8)$$

and

$$A = \left(\frac{\partial h_1}{\partial x}\right)_{p,T} \frac{y - x}{T_i \cdot c_{p,l}}$$

Eq. (7) was written for the interactions of the gas–liquid generation/absorption type, but if adequate indices are used it is also valid for the other types of solid–liquid or solid–gas two-phase two-component physical interactions where the phase changes. The sign of the force $(-X)$ was established so as to have a physical sense: in case of absorption the currents and forces are positive, therefore $(-X)_{\text{cpl,abs}} > 0$, and in case of generation they are negative, therefore $(-X)_{\text{cpl,gen}} < 0$ [1]. The typical aspect of a force described by Eq. (7) is shown in Fig. 1, for the $\text{NH}_3/\text{H}_2\text{O}$ system with physical absorption/generation interaction. For the case study, the ideal point (state) is at $x_{\text{ip}} = 0.3396$ (marked by the dotted vertical line). Gas mixture absorption takes place for liquid mass fractions strictly less than this value, while generation for values strictly higher than this value. We can remark that forces continuously increase in absolute value to maximal finite values approaching the ideal point, according to the natural force postulate [1]. The currents

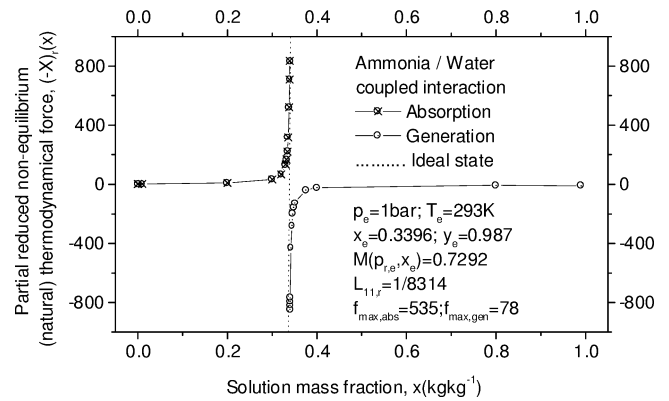


Fig. 1. Typical force behavior in case of a physical coupled interaction.

generated by these forces suffer an ideal point approaching (i.p.a.) effect [1]. The i.p.a. effect of a coupled transfer may be quantified, in case of a single type of interaction (e.g., absorption/condensation or generation/vaporization), by a figure of merit, “f”, equal to the ratio of two same type function values, corresponding to the states closer, respectively, farther to the ideal state (in the case at hand $f_{\text{max,abs}} = 535$ and $f_{\text{max,gen}} = 78$).

2. Interaction of pure component systems what change the phase.

$$(-X)_{\text{cpl,p}} = -(s' - s'') - \max(h', h'') \left(\frac{1}{T'} - \frac{1}{T''}\right) \quad (9)$$

Eq. (9) was obtained from Eq. (6), considering $n' = n'' = 1$ and the thermal balance at the level of the system for direct and reverse interaction $h' = h'' \pm j_q$, where j_q is in this case the latent heat of the phase change. Particularizing Eq. (9) for condensation or solidification processes, it results that

$$(-X)_{\text{cpl,c(s)}} = -(-X)_{\text{cpl,p}} > 0 \quad (10)$$

while, for vaporization or melting, it results that

$$(-X)_{\text{cpl,v(m)}} = (-X)_{\text{cpl,p}} < 0 \quad (11)$$

Typical behavior of force governing an interaction between pure component systems what change the phase is shown in Fig. 2 for nitrogen and oxygen vaporization/condensation. Again, ideal points position is marked by dotted vertical lines and forces respect the natural force postulate. However, while the interactions considered are once more of a physical type, the i.p.a. effect is this time much less pronounced, as compared to that of bi-component system interactions, Fig. 1.

3. Independent chemical interaction.

The force of an independent chemical interaction is given in detail in [1]. Its expression follows

$$(-X)_{\text{cpl,ch}} = -\left\{\sum_{i=1}^{n'} j'_{i,r} \left[s'_i + \max(h'_i, h''_i) \left(\frac{1}{T'_i} - \frac{1}{T_{\text{ip}}}\right)\right] - \sum_{i=1}^{n''} j''_{i,r} s''_i\right\} \quad (12)$$

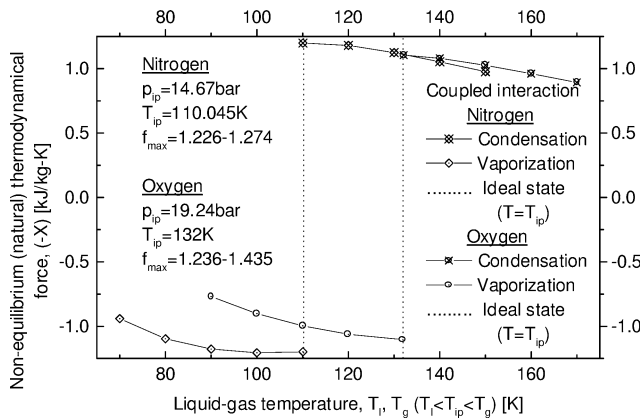


Fig. 2. Typical force behavior in case of a physical coupled gas-liquid interaction with pure systems.

As previously mentioned, the summation in Eq. (12) is over all systems of the global system, what here are called reactants, before reaction, and produces of reaction, after that. In the case of direct and reverse chemical reactions the next equations are valid

$$(-X)_{\text{cpl, ch, d}} = (-X)_{\text{cpl, ch}}$$

and

$$(-X)_{\text{cpl, ch, i}} = -(-X)_{\text{cpl, ch}} \quad (13)$$

respectively. A typical natural force graph of an independent chemical interaction is shown in Fig. 3. The case study analyses the natural force behavior around an ideal point ($T_{ip} = 973.15$) (or “equilibrium point” as it is well known from the literature) for three constant reaction pressures (T_{ip} and pressures are chosen at random), when methane interacts in the direct sense at temperatures $T < T_{ip}$ with oxygen to form carbon dioxide and water, and in the reverse sense carbon dioxide interacts at temperatures $T > T_{ip}$ with water to form methane and oxygen. Here the chemical interaction also benefits of an i.p.a. effect. Its figure of merit is higher than that of the pure component interactions, but is still much less than the f -value of bi-component systems [1].

Natural forces of non-coupled transfer. Non-coupled interactions are characterized by

$$\begin{aligned} n' &= n'' \\ j'_i &= j''_i, \quad i = 1, \dots, n' \\ j'_q &= 0 \\ v'_i &= v''_i, \quad A'_i \equiv A''_i, \quad i = 1, \dots, n' \end{aligned} \quad (14)$$

While involved mass and heat currents are non-null, as it can be remarked from Eqs. (14) in case of non-coupled interactions we do not expect to have mass transfer, but only heat and/or mechanical work transfer.

1. Heat exchange based interaction. The natural force of a heat exchange based non-coupled interaction is obtained from Eq. (12), by applying Eqs. (14). Such force is deemed to be negative or positive, whether the processes are of cooling, or of heating, respectively, and is given by [1]

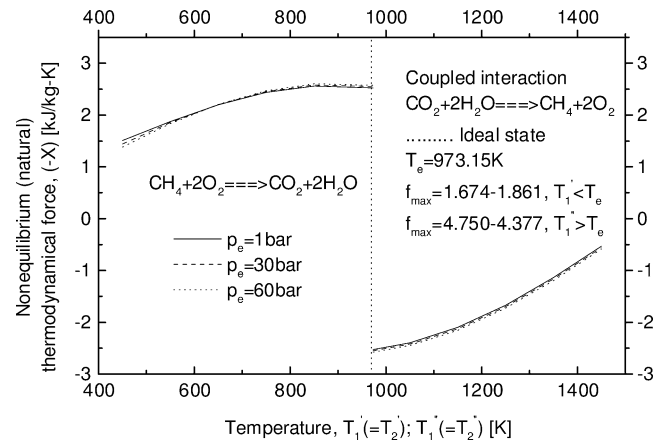


Fig. 3. Typical force behavior in case of an independent chemical interaction.

$$\begin{aligned} (-X)_{\text{ncpl}} &= - \sum_{i=1}^{n'} j'_{i,r} \left[(s'_i - s''_i) + \max(h'_i, h''_i) \left(\frac{1}{T'_i} - \frac{1}{T_{ep}} \right) \right] \end{aligned} \quad (15)$$

In case of interactions without sources, the unknown factor of the problem (the final equilibrium temperature T_{ep} or one of the currents) is calculated out of a simple thermal balance of the system in equilibrium given by the equation

$$\sum_{i=1}^{n'} j'_{i,r} c_{p,i} (T_{ep} - T'_i) = 0$$

Referring to interactions with a source, Eq. (15) holds true again and, as previously mentioned, the summation is over all systems interacting with that source through non-coupled transfer. If T_s is the source constant temperature, then in Eq. (15) we must consider $T_{ep} = T_s$.

As previously mentioned, the natural forces have a vector additive property. By using this property, the natural force of a non-coupled isobaric interaction may be expressed in a simpler form (see the ANNEX) by means of equation

$$(-X)_{\text{ncpl, s, p}} = - \sum_{i=1}^{n'} j'_{i,r} \left[\left(\frac{h}{T} \right)'_i - \left(\frac{h}{T} \right)_{\text{ep, i}} \right]_p \quad (16)$$

It can be easily demonstrated that Eq. (16) is also valid for $n' = 1$ in the case of the forces of coupled isobaric interactions with pure component systems (Eq. (9)). It is noted that the state function $(h/T) = s_t$ acquires a special significance in this context. For this reason, it will be referred to hereinafter as (*mass and heat transfer entropy*).

The typical forces aspect of such non-coupled transfer is the one shown in Figs. 4 and 5. For the sake of simplicity, in Eq. (16) we considered $n' = 1$. The two case studies refer to interactions of nitrogen and carbon dioxide with a constant temperature source, respectively. In this case the heat transfer is the classical conductive or convective one, proportional to the difference in temperature of the systems

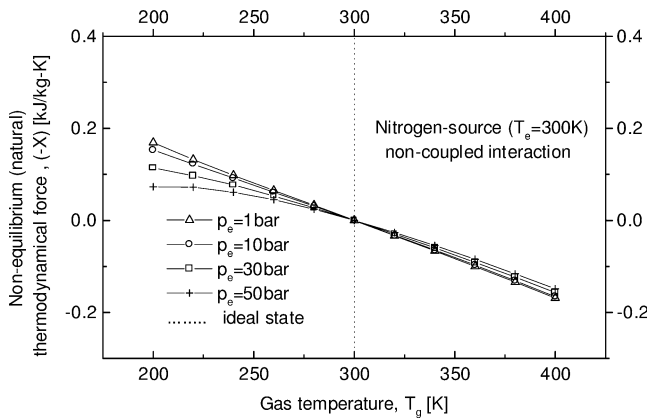


Fig. 4. Typical force behavior for a non-coupled interaction. Case study of nitrogen-source interaction.

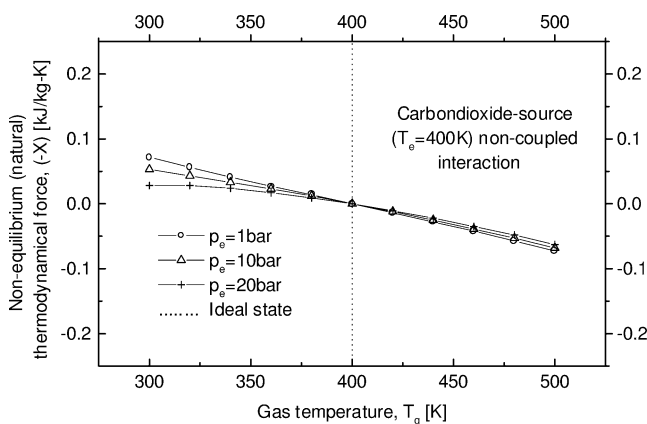


Fig. 5. Typical force behavior in case of a non-coupled interaction. Case study of carbondioxide-source interaction.

in a reasonable broad vicinity of the equilibrium point. Forces have a monotonous variation in the cooling $T > T_{ep}$ and heating $T < T_{ep}$ processes and take the value zero in the equilibrium points.

2. Mechanical work (power) exchange based interaction. Finally, the natural force of an adiabatic non-coupled interaction with a source will be established, that is the force whereby the systems of the global system exchange mechanical work (power) with a source. This force results from Eq. (4), assuming $j_q = 0$, given that the mechanical work is obtained by the consumption of the internal energy of the systems interacting with the source, having parameters (p_{ep}, T_{ep})

$$(-X)_{ncpl,w} = - \sum_{i=1}^{n'-1} j'_{i,r} (e'_i - e''_i) \quad (17)$$

where

$$e = s + \frac{h}{T} \quad (18)$$

Coupled/non-coupled transfer general characteristics. Because, according to the postulate and its consequence (i.p.a.

effect), forces and currents continuously increase in absolute value to maximal finite values approaching an ideal point, the coupled transfer of mass and heat is a fast (“accelerated”) transfer. Unlike these systems, the non-coupled interaction systems evolve towards an equilibrium point under the action of natural forces that tend to zero and have value zero in this point. The resulting mass and heat currents preserve the characteristic of the force and do not benefit by the i.p.a. effect. That is why the non-coupled transfer is a slow (“decelerated”) transfer.

3. System-source interactions

Given that non-coupled transfer is slow, it is preferable to be avoided in power installations. The extents to which this can be achieved and the relation between the two types of transfer referred to above when a system and a source, as constitutive parts of the global system, interact one to the other, are presented hereinafter. To the beginning, the following first basic theorem will be demonstrated [5].

Theorem (Of the equilibrium (absolute) point). *A mono-component or poly-component system and a source (infinite reservoir) of constant parameters may evolve and reach equilibrium together only by a non-coupled mass and heat transfer.*

Demonstration. It will be first demonstrated by means of the reductio ad absurdum method that the system and the source cannot be in equilibrium by a coupled transfer. Basically, sources are considered to preserve unaltered their physical state and parameters during any interaction with systems. For the sake of clarity only, here we shall consider that our source is an infinite heat reservoir of constant temperature T . It is assumed that the system is in equilibrium with the source by a coupled transfer. In this case, their interaction results in either a change of phase (nature) of the source, what is absurd, or it follows that the source, according to the corollary in [1], is not defined in $t = T$, but fluctuates at equilibrium between $T - \Delta T$ and $T + \Delta T$, where ΔT is a finite difference of temperature, which is again absurd, contradicting the hypothesis according to which T is constant and thus the first part of the theorem is demonstrated. A first conclusion what can be drawn out of the above is that at equilibrium the force and the currents of this interaction are annulled. In order to demonstrate that the system and the force not even cannot evolve together towards equilibrium by coupled transfer, it is sufficient to remind that, according to the postulate, the system would tend towards equilibrium with the source by forces and currents continuously growing towards maximum finite absolute values, which are not annulled in the ideal point. This is absurd, as it contradicts the conclusion of the first part of the demonstration, and thus the theorem is demonstrated.

The theorem is also valid in the event that the system evolving towards equilibrium with the source goes through various phases where coupled transfer also occurs. Let us assume, for instance, a gaseous system what is isobar cooled in its interaction with a sink source $T_s (= T_{ep})$ from temperature T_g to temperature $T_l (= T_{ip} - 0.0)$, at which temperature it condenses, and the condensate is sub-cooled up to T_s , when reaches the equilibrium. The temperatures involved in this process are, as it can be noticed, in the relation $T_g > T_{ip} > T_l \geq T_s$. The coupled transfer of gas (cooling + condensation) and mixed [(gas (cooling + condensation) + liquid sub-cooling)] are described by the natural forces given by Eq. (9)

$$(-X)_{cpl,c} = (s_g - s_l) + h_g \left(\frac{1}{T_g} - \frac{1}{T_l} \right) > 0, \quad (19)$$

$$T_l = T_{ip} - 0.0$$

and

$$(-X)_{mixed,c} = (s_g - s_{ep}) + h_g \left(\frac{1}{T_g} - \frac{1}{T_{ep}} \right) > 0 \quad (20)$$

respectively. If Eq. (20) is subtracted from Eq. (19), the result is a force of the Eq. (15) type

$$(-X)_{ncpl,c} = -(s_l - s_{ep}) - h_g \left(\frac{1}{T_l} - \frac{1}{T_{ep}} \right) < 0 \quad (21)$$

what is just the force of the non-coupled transfer process stipulated by the theorem. The non-coupled transfer is adjacent to the source and interposes between the source and the coupled process described by Eq. (9). This configuration of transfer with a source is general. It always appears whenever a mixed transfer process takes place. Developing the given example for the reversed process, of vaporization, the liquid warms isobar as a result of the interaction with a warm source $T_s (= T_{ep})$, from temperature T_l to temperature $T_g = T_{ip} + 0.0$. At this temperature it vaporizes, and the resulting vapor is superheated up to T_s , when reaches the equilibrium. The temperatures involved in the process are in the relation $T_l < T_{ip} < T_g \leq T_s$. The homologous equations to Eqs. (19)–(21) are the following

$$(-X)_{cpl,v} = -(s_g - s_l) - h_g \left(\frac{1}{T_g} - \frac{1}{T_l} \right) = -(-X)_{cpl,c} < 0, \quad T_g = T_{ip} + 0.0 \quad (22)$$

$$(-X)_{mixed,v} = -(s_{ep} - s_l) - h_g \left(\frac{1}{T_{ep}} - \frac{1}{T_l} \right) < 0 \quad (23)$$

and

$$(-X)_{ncpl,v} = -(s_g - s_{ep}) - h_g \left(\frac{1}{T_g} - \frac{1}{T_{ep}} \right) > 0 \quad (24)$$

respectively. From Eqs. (19)–(21) or (22)–(24) and in accordance with Eq. (2), it is noted that the force of the mixed transfer has additive properties as compared to the partial forces of the coupled, respectively, non-coupled

transfer. Generalizing, the following vector equation is obtained

$$(-\vec{X})_{mixed} = (-\vec{X})_{cpl} - (-\vec{X})_{ncpl} \quad (25)$$

what is valid for all two-phase interactions with mixed transfer where the coupled transfer results from a physical or a chemical interaction (Eqs. (7)–(13)). Coming back to the previous examples, for a certain chosen gas and pre-established temperatures T_g or T_l and T_s , the $(-X)_{mixed}$ force has a determined value. A simple analysis of the two terms of the right member of Eq. (25) shows that forces have contrary signs (see also Figs. 6 and 7), but the non-coupled and coupled transfers do not have contrary effects. This observation precedes the making evident of a more general property of the mixed transfer. In order to identify such property, the following second basic theorem must be first demonstrated

Theorem (Concerning the existence and uniqueness of the ideal (relative) point). *If a system interacts with a source (infinite reservoir) by mixed stationary mass and heat transfer, then the constitutive processes, of coupled and non-coupled transfer, respectively, are always separated by an ideal (relative) point which is unique.*

Demonstration. The reductio ad absurdum method will be used. We assume a system that interacts with a source by mixed transfer. In order to demonstrate the existence of the ideal point, we assume, contrary to all reason, that there is no ideal (relative) point separating the coupled transfer from the non-coupled one in the interaction of the system with the source. Then the only point controlling the interaction is the equilibrium (absolute) point, established by the source, and in accordance with the theorem of the equilibrium point the transfer is not mixed, but only non-coupled, which contradicts the hypothesis and therefore the existence of the ideal point is demonstrated. The reciprocal statement is evidently true. In order to demonstrate the uniqueness of the ideal point, it is assumed that beside the first ideal point identified, there is also a second. Then, according to the reciprocal of the existence of the ideal point, it follows that after outrunning the first ideal point, the system evolves again towards the equilibrium point by a mixed transfer, so that its natural force moves from the first ideal point to the second by having continuously increasing values in absolute value, according to the postulate of the natural force of the coupled transfer, set forth in [1]. We will now imagine that the system evolves in the reverse direction. This leads to the conclusion that the coupled transfer process which takes place from the second ideal point to the first is characterized by natural forces continuously decreasing in absolute value, which is absurd, contradicting the postulate of the natural force referred to above. Thus the uniqueness of the ideal point, as well as the entire theorem, is demonstrated.

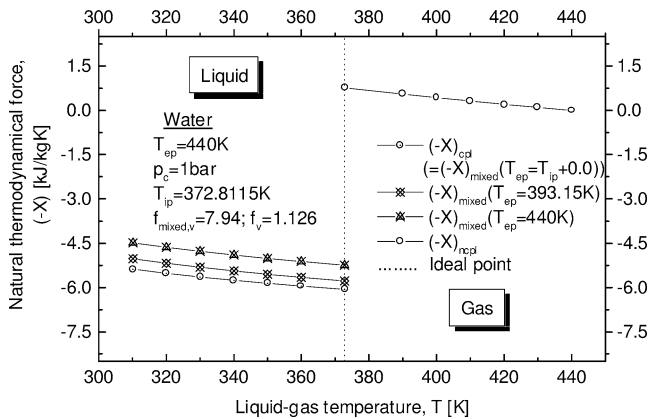


Fig. 6. Study case of natural forces of a mixed transfer in water [liquid (heating + vaporization) + gas super-heating].

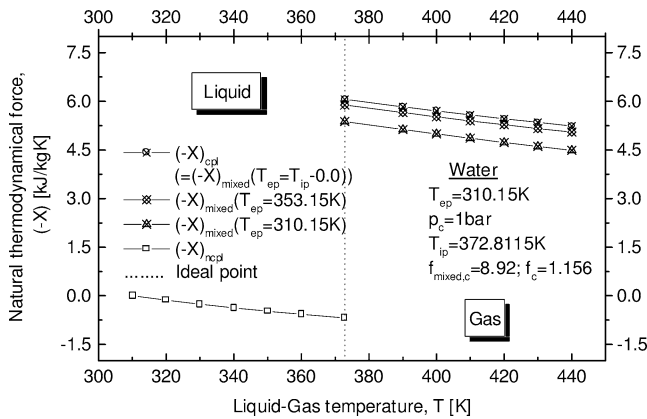


Fig. 7. Study case of natural forces of a mixed transfer in water [gas (cooling + condensation) + liquid sub-cooling].

It follows that a system with mixed transfer cannot contain two or more coupled transfers in series. Indeed, as we already know from the experimental physics, this means that if a system is subjected to a mixed transfer where the distance between the ideal point and the equilibrium point is sufficiently big so that the system is forced to undergo more than a change of phase, then it passes directly from the first phase to the last one, which corresponds to the equilibrium with the source, without going through the intermediary phase changes (e.g., the mixed transfer by sublimation or de-sublimation).

As a conclusion of the foregoing, it can be stated that non-coupled transfer systems may reach equilibrium with sources by reversible transformations round the equilibrium point, to which, according to Eq. (3), the null velocities of exergy destruction ($\dot{A}(z_{ep}) = 0$) correspond. On the contrary, coupled transfer systems can never reach equilibrium with sources and that is why their transformations are irreversible, far from equilibrium, and reach maximum values of exergy destruction in the vicinity of the ideal points. In other words, equilibrium is not possible but only with the sources.

Now, taking into consideration the above theorem and the lemma demonstrated in [1], the following corollary could be formulated

Corollary. *If a system evolves towards the equilibrium dictated by a source through a mixed mass and heat transfer, then natural forces of partial coupled and non-coupled transfers composing it have always contrary signs.*

The above examples will be particularized to a case study of two mixed transfers in water at normal pressure: (i) (liquid heating + vaporization), Fig. 6, and (ii) (condensation + liquid cooling), Fig. 7. Natural forces describe them subject to the temperatures of the liquid and gas. In Fig. 6, source equilibrium point is $T_{ep} = 440$ K. The system evolves towards this point through a coupled transfer of liquid heating and vaporization at $T_g = T_{ip} (= 372.8115 \text{ K}) + 0.0$ (see $(-X)_{cpl}$), and non-coupled of gas superheating, whereby, in accordance with the equilibrium point theorem, it reaches equilibrium at $T_g = T_{ep} = 440$ K (see $(-X)_{ncpl}$). Approaching T_{ep} and T_{ip} , force of the entire process $(-X)_{mixed}$ increases in absolute value (see $(-X)_{mixed}$ at $T_{ep} = 393.15$ K and $T_{ep} = 440$ K). To the limit, when $T_{ep} = T_{ip} + 0.0$, we have the greatest absolute value of mixed force, $(-X)_{mixed} = (-X)_{cpl}$. It is noted that, in accordance with the ideal point theorem corollary and Eq. (11), forces have contrary signs, $(-X)_{cpl,v} < 0$ and $(-X)_{ncpl} > 0$, and the two transfers are separated by an ideal vaporization point with unequal branches, around which $|(-X)_{cpl}| \gg (-X)_{ncpl}$. Proceeding similarly as to the i.p.a. effect evaluation, in the case of the mixed transfer a merit factor which quantifies the difference between the forces adjacent to an ideal point could also be introduced,

$$f_{mixed} = \left| \frac{(-X)_{cpl}(z_{ip} \pm 0.0)}{(-X)_{ncpl}(z_{ip} \mp 0.0)} \right| \quad (26)$$

Here $f_{mixed,v} = 7.94$ and for i.p.a. effect $f_v = 1.126$. Eq. (26) prefigures the advantage of using the coupled transfer in transport phenomena, as compared to the non-coupled transfer (conductive or convective) (see the heat pipe [5,6]).

In Fig. 7, source has $T_{ep} = 310.15$ K. The system evolves towards this point by a coupled transfer of gas cooling and condensation at $T_l = T_{ip} (= 372.8115 \text{ K}) - 0.0$ (see $(-X)_{cpl}$) and non-coupled of liquid sub-cooling, up to equilibrium at $T_l = T_{ep} = 310.15$ K (see $(-X)_{ncpl}$). Approaching T_{ip} and T_{ep} , then again $(-X)_{mixed}$ increases, approaching $(-X)_{cpl}$ (see $(-X)_{mixed}$ at $T_{ep} = 310.15$ K and $T_{ep} = 353.15$ K). To the limit, when $T_{ep} = T_{ip} - 0.0$, we have the greatest mixed force $(-X)_{mixed} = (-X)_{cpl}$. Forces signs are different here too, $(-X)_{cpl,c} > 0$ and $(-X)_{ncpl} < 0$, and the two transfers are separated by an ideal vaporization point with unequal branches, where $|(-X)_{ncpl}| \ll (-X)_{cpl}$, so that $f_{mixed,c} = 8.92$ (Eq. (26)) and $f_c = 1.156$.

4. Phenomenological coefficients of mixed transfer and the theorem concerning the maximization thereof

The mass and heat currents are calculated from the phenomenological point of view by means of equations [1,2]

$$(\vec{j}_i)_{\text{phenom}} = L(-\vec{X}) \quad (27)$$

and

$$(\vec{j}_q)_{\text{phenom}} = (\vec{j}_i)_{\text{phenom}} C = L(-\vec{X})C \quad (28)$$

respectively, what are valid for the coupled, non-coupled or mixed transfer. In Eq. (28), C stands for the thermal capacity. In the case of a bi-component system physically interacting with one source only, C is given by [1,2]

$$C = (h'(z) - h''(z)) - (y - x) \left(\frac{\partial h'(z)}{\partial x} \right)_{p,T} \quad (29)$$

In the case of a system interacting with different sources between two states the forces are modified accordingly and $C = h$.

According to the phenomenological equilibrium theory, the phenomenological forces and coefficients are deemed to be weakly dependent on each other. The relation between the natural force and the phenomenological coefficient is maintained here too. The phenomenological coefficient depends on the thermal properties and the dynamics of the interacting elements [1,2]. The phenomenological coefficients involved in a mixed transfer will be established in this section. For the sake of clarity, the calculation will be particularized to the mixed transfer of (gas (cooling + condensation) + liquid sub-cooling), without diminishing the generality of the results. Indeed, Eqs. (27)–(29) are taken into account and the mass and heat currents of the transfer are written in accordance with Eq. (25), what leads to

$$L_{\text{mixed}}(-\vec{X})_{\text{mixed}} = L_{\text{cpl}}(-\vec{X})_{\text{cpl}} - L_{\text{ncpl}}(-\vec{X})_{\text{ncpl}} \quad (30)$$

and

$$\begin{aligned} L_{\text{mixed}}(-\vec{X})_{\text{mixed}}(h_g - h_{\text{ep}}) \\ = L_{\text{cpl}}(-\vec{X})_{\text{cpl}}(h_g - h_l) - L_{\text{ncpl}}(-\vec{X})_{\text{ncpl}}(h_l - h_{\text{ep}}) \end{aligned} \quad (31)$$

respectively. Eqs. (30) and (31) are solved together with Eqs. (25) and (26), assuming that forces $(-\vec{X})_{\text{cpl}}$ and $(-\vec{X})_{\text{ncpl}}$ are collinear and we obtain

$$L_{\text{ncpl}} = -L_{\text{cpl}} f_{\text{mixed}} r_h < 0 \quad (32)$$

and

$$L_{\text{mixed}} = L_{\text{cpl}} \frac{f_{\text{mixed}}}{1 + f_{\text{mixed}}} (1 - r_h) > 0 \quad (33)$$

where

$$r_h = \frac{\min |h(z_{\text{ep}}) - h(z_{\text{ip}} \pm 0.0)|}{\max |h'(z) - h(z_{\text{ip}} \pm 0.0)|} > 0 \quad (34)$$

Eqs. (32) and (33) are valid for all interactions with mixed transfer. The phenomenological coefficient of the coupled

transfer of a physical or chemical nature, L_{cpl} , must be established prior to calculating L_{ncpl} and L_{mixed} . In the case of (ideal) gas (')-liquid (") [1,2], (ideal) gas (')-solid (") and liquid (')-solid (") interactions, this coefficient has the expression

$$L_{\text{cpl}} = \frac{j_r}{(-X)_{\text{cpl}}} j_i'' > 0 \quad (35)$$

where

$$j_r = \pm \frac{p'}{\rho'' c_v' T'}$$

or

$$j_r = \pm \frac{\rho'}{\rho''} \quad (36)$$

and $j_i'' = \rho'' |\dot{V}'|$ is established for phenomenological and dynamic reasons [7]. The above results allow us to highlight the characteristics of the mixed transfer itself and in comparison with the non-coupled transfer. Indeed, let us to establish the ratio of the mass and heat currents of mixed and non-coupled transfer involved in the interaction with the source previously used

$$r_i = \left(\frac{j_{i,\text{mixed}}}{j_{i,\text{ncpl}}} \right) = \frac{L_{\text{mixed}}(-X)_{\text{mixed}}}{L_{\text{ncpl}}(-X)_{\text{ncpl}}} \quad (37)$$

and,

$$r_q = \left(\frac{j_{q,\text{mixed}}}{j_{q,\text{ncpl}}} \right) = \frac{L_{\text{mixed}}(-X)_{\text{mixed}}(h_g - h_{\text{ep}})}{L_{\text{ncpl}}(-X)_{\text{ncpl}}(h_l - h_{\text{ep}})} \quad (38)$$

respectively. If Eqs. (32)–(34) are taken into consideration, then Eqs. (37) and (38) are rewritten as follows

$$r_i = \frac{1 - r_h}{r_h} \quad (39)$$

and,

$$r_q = \frac{1 - r_h^2}{r_h^2} \quad (40)$$

respectively. Given that

$$\lim_{z_{\text{ep}} \rightarrow z_{\text{ip}}} r_h = 0 \quad (41)$$

it follows that the ratios r_i and r_q are maximized for $z_{\text{ep}} \rightarrow z_{\text{ip}}$. Fig. 8 shows the effect of the initial temperature of the liquid and of the distance between the ideal point and the equilibrium point on the r_q ratio in the case of water vaporization at normal pressure. On the other hand, taking into account Eqs. (27), (28), (32), (35) and (41), it is noted that

$$\lim_{z_{\text{ep}} \rightarrow z_{\text{ip}}} j_{i,\text{ncpl}} = 0 \quad (42)$$

and

$$\lim_{z_{\text{ep}} \rightarrow z_{\text{ip}}} j_{q,\text{ncpl}} = 0 \quad (43)$$

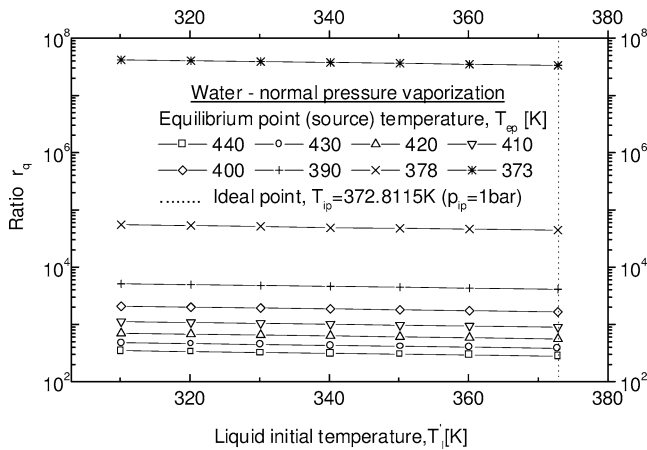


Fig. 8. The effect of the liquid initial temperature and of the distance equilibrium point-ideal point on ratios r_l and r_q in case of water at normal pressure.

so that, based upon the consequence of the natural force postulate

$$\max |j_{i,mixed}| = \lim_{z_{ep} \rightarrow z_{ip}} j_{i,mixed} = j_{i,cpl}(z_{ip} \pm 0.0) \quad (44)$$

and

$$\max |j_{q,mixed}| = \lim_{z_{ep} \rightarrow z_{ip}} j_{q,mixed} = j_{q,cpl}(z_{ip} \pm 0.0) \quad (45)$$

Thus, the following theorem has been demonstrated

Theorem (Concerning the maximization of the mixed transfer). *If a system interacts with a source by mixed transfer, the mass and heat currents are maximized in absolute value and in relation with the non-coupled currents when the equilibrium point tends towards the ideal point.*

Bearing in mind the problem raised at the beginning of Section 3, theorem of the equilibrium point shows that, although it is slow, the non-coupled transfer is unavoidable in a power installation connected to sources. However, wherever possible, theorem of the mixed transfer maximization indicates that this drawback could be diminished by conveniently replacing the non-coupled transfer with a mixed one. Efficient energetic plants already apply it, although this arises more from a valuable empirical experience than from a rigorous proof.

Eq. (38) demonstrates that the i.p.a. effect is the main responsible for the increase of heat exchange with a source in the case of a mixed transfer. Its highlighting seems to be the key of clarifying coupled (mixed) mass and heat transfer phenomena that are difficult to be explained by the classic heat and mass transfer approach. This is the case of the refrigerating agent-absorbent systems interactions (e.g., ammonia/water [1,2]), or of the heat transfer mechanism in heat pipes, as it will be shown in the next work section, as a first application of the TPT.

5. Application of TPT to the thermodynamic cycles

5.1. Theoretical aspects

The TPT may contribute to the analysis and optimization of the thermodynamic cycles. A cycle has a certain number of meaningful points $(p, T, x, y, \dots)_1, \dots, (p, T, x, y, \dots)_n$ (degrees of freedom) characterizing the inlets/outlets and evolution of a mono-, bi-, or poly-component/phase working fluid. The working fluid covers the cycle component devices where undergoes mass, heat, and work transfer processes. The processes are considered to be of non-coupled and/or mixed nature. Each device houses a global system where the working fluid materializes the multitude of systems interacting one to each other and with sources, connected to devices. While many times, not all, sources interact in fact indirectly with the working fluid through appropriate parts of the devices, here in our applications a direct contact fluid-source will be considered. Taking advantage of these statements, the following balances on the working fluid will be written in a cycle:

- property of conservation of the natural force $(-X)$, as a state function [1,2]

$$\oint d(-X) = 0 \quad (46)$$

- mass conservation law

$$\oint d(L(-X)) = 0 \quad (47)$$

- first principle of thermodynamics

$$\oint d(LC(-X)) = 0 \quad (48)$$

The Eqs. (46)–(48) are valid for any type of natural forces presented in the second section of this paper, which describe physical, chemical, work etc. interactions. If cycle energy exchanged with the source is explicitly expressed in Eq. (48), the following expression is obtained

$$\oint d(LC(-X)) = \dot{W} \quad (49)$$

what is also used hereinafter. Eq. (46) was applied in [1] to demonstrate the lemma for an isolated system, as well. Here, if separate mixed and non-coupled transfers occur in the cycle, Eq. (46) is rewritten under the particular form as

$$\oint d[(-X)_{mixed} + (-X)_{ncpl,s}] = 0 \quad (50)$$

When, beside the non-coupled forces, the coupled natural forces also intervene in the transfer, the cyclic evolution of the working fluid requires

$$\oint d(-X)_{cpl} = 0 \quad (51)$$

Combining Eqs. (50) and (51), it follows that

$$\oint d(-X)_{\text{ncpl}} = 0 \quad (52)$$

Eqs. (46)–(48) can be useful in the first steps of a certain cycle design. Suppose a cycle to be conceived, thermodynamically speaking, Eqs. (48)–(49), already applied in their classic form, reduce the degree of freedom of the cycle. The phenomenological Eqs. (46)–(47) show that the degree of freedom of the cycle connected to sources must be further reduced, provided that no other additional constraints exist.

Next we shall apply the TPT to two simple study cases. As we will remark, at this stage of development this new theory will confine to reveal only some of its main qualities in the study of cycle basic thermodynamic properties and suggest what type of applications could be used in the future to.

5.2. Application to a heat pipe type cycle

Heat pipes are largely used today in energetic installations, [6]. The literature presenting their detailed thermohydrodynamic modeling and experimental work is also very rich, where from some recent papers are cited [8–10]. However, while the benefic role of the working fluid vapor as a rapid energy carrier between evaporator and condenser is well understood so far, not yet the evaporator/condenser heat transfers taking place with intrinsic high values are satisfactorily explained when the internal heat pipe heat transfer is discussed. Indeed, keeping our notations, the heat transfer is classically assessed in a mixed interaction of vaporization/condensation type by the empiric equation [11–14]

$$(j_q)_{\text{classic}} = \alpha S \max |(T_{\text{ip}} \pm \varepsilon) - T_{\text{ep}}| \quad (53)$$

where α and S are a coefficient of heat transfer and the transfer area, respectively. In principle, Eq. (53) may be not useful in the prediction of the transferred power at the heat pipe evaporator/condenser $(j_q)_{\text{classic}}$, simply because α is an empiric dimension. On the contrary, Eq. (53) is utilized to determine the α value in a second step through a current method what in a first step experimentally finds the transferred heat power and the working fluid temperature differences. Moreover, from the TPT point of view, Eq. (53) also lacks the physical support in order to assess a mixed transfer, because $(j_q)_{\text{classic}} \rightarrow 0$ when $T_{\text{ep}} \rightarrow T_{\text{ip}}$ and thus it contradicts the mixed transfer maximization theorem. To these extents, making a parenthesis, it can be noticed that, as expected, the distance $\max |(T_{\text{ip}} \pm \varepsilon) - T_{\text{ep}}|$ is not factorable in the phenomenological Eqs. (20) and (23), describing the mixed transfer for pure components. In the frame of the TPT, the only transfer where this distance is factorable is the pure non-coupled one. Indeed, in this case $T_{\text{ip}} \pm \varepsilon$ becomes the temperature of the heated (cooled) fluid up to nearly T_{ep} without a change of phase and if this temperature is further written down as T_f , from Eqs. (15) and (27), for sufficiently small $T_{\text{ep}} - T_f$ distances it results that

$$(j_q)_{\text{phenom}} = (\alpha S)_{\text{phenom}} (T_{\text{ep}} - T_f) \quad (54)$$

where

$$(\alpha S)_{\text{phenom}} = LC \left[\left(\frac{\partial s}{\partial T} \right)_p - \frac{\max(h', h'')}{T_f T_{\text{ep}}} \right] \quad (55)$$

Reverting to the problem at hand, given the remarks outlined above, in the followings we shall use the TPT to explain the real basic thermodynamic reason of the high heat transfer capability of a heat pipe type cycle. To do this, a simple mathematical apparatus will be used, applying Eqs. (46)–(50) to a case study of mass and heat transfer of water in a cyclic evolution between two sources, characterized by the equilibrium point of vaporization $z_{\text{ep},v} = T_{\text{ep},v}$ and, respectively, of condensation $z_{\text{ep},c} = T_{\text{ep},c}$. The cycle exchanges heat only with the two sources, the transfer is only mixed and does not produce mechanical work useful in the exterior. In principle, it is therefore similar to the one of a heat pipe. Under the circumstances, Eq. (50) is written as follows

$$(-X)_{\text{mixed},v} + (-X)_{\text{mixed},c} = 0 \quad (56)$$

or, accounting for Eqs. (23) and (20),

$$\begin{aligned} & \left\{ -[s(T_{\text{ep},v}) - s(T_{\text{ip},c} - \varepsilon)] \right. \\ & \quad \left. - h(T_{\text{ip},v} + \varepsilon) \left(\frac{1}{T_{\text{ep},v}} - \frac{1}{T_{\text{ip},c} - \varepsilon} \right) \right\} \\ & + \left\{ [s(T_{\text{ip},v} + \varepsilon) - s(T_{\text{ep},c})] \right. \\ & \quad \left. + h(T_{\text{ip},v} + \varepsilon) \left(\frac{1}{T_{\text{ip},v} + \varepsilon} - \frac{1}{T_{\text{ep},c}} \right) \right\} = 0 \end{aligned} \quad (57)$$

where $T_{\text{ip},v} = T_{\text{ip},v}(p_{\text{ep},v})$ and $T_{\text{ip},c} = T_{\text{ip},c}(p_{\text{ep},c})$ are the ideal points of vaporization and, respectively, condensation, and $\varepsilon = 0.0$. A second equation of the case study is obtained if Eqs. (56) and (47) are taken into consideration. From here, with Eqs. (26), (32), (33), (35) and (51), it follows that

$$[j_r(1 - r_h)]_v + [j_r(1 - r_h)]_c = 0 \quad (58)$$

and further, with Eq. (34)

$$\begin{aligned} & [h(T_{\text{ip},v} + \varepsilon) - h(T_{\text{ep},v})]_v \\ & + [h(T_{\text{ip},c} - \varepsilon) - h(T_{\text{ep},c})]_c = 0 \end{aligned} \quad (59)$$

Eq. (59) might have been directly obtained by applying Eq. (47) to Eq. (49), where $\dot{W} = 0$. Eqs. (57) and (59) represent an implicit algebraic system at unknowns $T_{\text{ip},v} + \varepsilon$ and $T_{\text{ip},c} - \varepsilon$. Before solving this system, generally, it is noted that, an always strictly positive distance between the equilibrium point and the ideal point characterizes a system connected to a source by mixed transfer

$$\|z_{\text{ep}} - z_{\text{ip}}\| > 0 \quad (60)$$

for any $z_{\text{ep}} \in D$, with $(-X)_{\text{mixed}} : D$, because $z_{\text{ip}} \notin D$ [1,2]. Equally, $(\exists)\varepsilon > 0$, so that

$$\min \|z_{\text{ep}} - (z_{\text{ip}} \pm \varepsilon)\| > 0 \quad (61)$$

From Eqs. (60) and (61), it results therefore that temperatures of the ideal and equilibrium points must be in the relation below

$$T_{ep,c} < T_{ip,c} - \varepsilon \leq T_{ip,v} + \varepsilon < T_{ep,v}$$

Even if in certain applications we could have $T_{ip,v} \cong T_{ip,c}$, it can be noted from the above relation that isothermal transfer is impossible. To this extent, the isothermal defect considered in classic heat pipe theory [6], is in fact not at all costs a consequence of the imperfect achievement thereof in practice, but an intrinsic property of the cyclic evolution of a fluid connected to sources, emphasized here in a phenomenological way.

It is difficult to analytically solve the system made up of Eqs. (57) and (59). In order to obtain the solution, an error and trial method and a commercial code suitable for the calculation of thermodynamic functions of state and of algebraic solution were used, [15]. The results obtained as unique solutions with absolute errors below 1% for various domains of water temperatures and various distances between equilibrium points, are shown in Table 1. Strictly depending on $T_{ep,v}$, $T_{ep,c}$ and on the nature of the fluid, they reveal the basic (bare) heat pipe cycle property explaining its high heat transfer: while the distances between the equilibrium points are by one or two magnitude orders bigger, the distances $\min \|z_{ep} - (z_{ip} \pm \varepsilon)\|$ are very small, quantified here at a minimum value, what according to the mixed transfer maximization theorem leads to a very good mixed transfer (which fact is pointed out by the $r_{q,c}(=r_{q,v})$ values, also shown in Table 1). Our explanation remains valid if real heat pipes are considered, where the

distances $\min \|z_{ep} - (z_{ip} \pm \varepsilon)\|$ resulting from the solving of the system will be altered, getting bigger due to the intervention of additional non-coupled forces (e.g., those governing the transfer through walls and liquid working fluid + its transporting capillary structure) or forces of a different nature, such as Laplace, gravitational, etc., resulting in a reduction of the mass and heat transfer (lower $r_{q,c}(=r_{q,v})$ values). We can remark that the i.p.a. effect again lays at the basis of explaining a mixed transfer based process, what this time is the high heat transfer of the heat pipe. A previous work [5] thoroughly studying the evaporative heat transfer in capillary grooved heat pipes, is confirming this statement. Indeed, although the result passed not remarked by the work author, from [5] it follows that the vaporization heat current reaches its maximum at the minimum T_{ep} temperatures of the evaporator wall, that is the temperatures which are closest to T_{ip} , in good agreement with the mixed transfer maximization theorem.

5.3. Role of natural forces conservation property. Application to the CAN theory

A second application emphasizes the importance of the Eq. (46). Its introduction is beneficial as it completes the application of the second principle of thermodynamics in the thermodynamics of cycles. It is more general than the well-known equation

$$\oint ds = 0 \quad (62)$$

Table 1

Phenomenological results of mixed mass and heat transfer in case of water suffering a heat pipe type cyclic evolution between two sources

| $t_{ep,v} - t_{ep,c}$ (°C) | $t_{ep,v}$ (°C) | $t_{ep,c}$ (°C) | $t_{ip,v}$ (°C) | $t_{ip,c}$ (°C) | $t_{ep,v} - t_{ip,v} - \varepsilon$ (°C) | $t_{ip,c} - t_{ep,c} - \varepsilon$ (°C) | $10^{-8} \times r_{q,c}$ ($=r_{q,v}$) | Absolute error | |
|-------------------------------|--------------------|--------------------|--------------------|--------------------|---------------------------------------------|---------------------------------------------|--------------------------------------------|-----------------------------------------------------|------------------------------------|
| | | | | | | | | Eq. (47) (kJ·kg ⁻¹ ·K ⁻¹) | Eq. (49) (kJ·kg ⁻¹) |
| 1 | 50 | 49 | 49.87 | 49.10 | 0.06 | 0.03 | 3.63 | 0.030 | 0.010 |
| | 60 | 59 | 59.87 | 59.10 | 0.06 | 0.03 | 3.55 | 0.021 | 0.008 |
| | 80 | 79 | 79.87 | 79.10 | 0.06 | 0.03 | 3.38 | 0.012 | 0.006 |
| | 90 | 89 | 89.86 | 89.10 | 0.08 | 0.04 | 1.85 | 0.013 | 0.005 |
| | 100 | 99 | 99.85 | 99.10 | 0.09 | 0.04 | 1.80 | 0.011 | 0.002 |
| 5 | 85 | 80 | 84.86 | 80.10 | 0.08 | 0.04 | 1.90 | 0.013 | 0.006 |
| | 90 | 85 | 89.85 | 85.10 | 0.10 | 0.05 | 1.20 | 0.015 | 0.006 |
| | 95 | 90 | 94.96 | 90.10 | 0.08 | 0.04 | 1.86 | 0.011 | 0.004 |
| | 100 | 95 | 99.86 | 95.10 | 0.08 | 0.04 | 1.83 | 0.010 | 0.002 |
| | 155 | 150 | 154.85 | 150.10 | 0.11 | 0.06 | 0.67 | 0.005 | -0.007 |
| | 160 | 155 | 159.86 | 155.10 | 0.10 | 0.06 | 1.20 | 0.015 | 0.006 |
| | 205 | 200 | 204.87 | 200.10 | 0.09 | 0.06 | 0.52 | 0.002 | 0.001 |
| | 210 | 205 | 209.87 | 205.10 | 0.09 | 0.06 | 0.51 | 0.002 | -0.004 |
| 10 | 60 | 50 | 59.94 | 50.05 | 0.12 | 0.01 | 33.03 | 0.004 | 0.003 |
| | 70 | 60 | 69.95 | 60.05 | 0.11 | 0.01 | 0.01 | -0.0 | -0.0 |
| | 80 | 70 | 79.95 | 70.05 | 0.11 | 0.01 | 0.01 | -0.0 | -0.0 |
| | 90 | 80 | 89.85 | 80.10 | 0.10 | 0.05 | 1.22 | 0.012 | 0.006 |
| | 100 | 90 | 99.84 | 90.10 | 0.12 | 0.06 | 0.83 | 0.012 | 0.003 |
| | 160 | 150 | 159.86 | 150.10 | 0.10 | 0.06 | 0.68 | 0.003 | 0.012 |
| | 210 | 200 | 209.87 | 200.10 | 0.09 | 0.06 | 0.52 | 0.002 | -0.006 |

what is valid only for reversible cycles [3]. Eq. (46) proves useful especially in the calculation of the irreversible cyclic transfer, where Clausius integral [3],

$$\oint \frac{dq}{T} < 0 \quad (63)$$

cannot be practically used. Hereinafter Eq. (46) will be used for a brief phenomenological assessment of the Curson–Ahlborn–Novikov (CAN) theory [13,16–21]. Originally, the CAN theory aimed at the power maximization of the Carnot cycle, subject to optimization of its finite-time heat transfer with sources. Later, the basic idea of this theory extended also to other cycles of work or heat pumping type [13]. First of all, phenomenologically, only pure non-coupled transfer with sources should be considered from the CANs theory point of view in a cycle including both mixed and non-coupled transfer with sources, because, according to the results outlined in Section 4 of this work (see third theorem), in case of the mixed transfer, cycle carnotization and finite-time heat transfer maximization occur simultaneously, when the working fluid temperatures approach those of the sources. Next, we assume the Carnot 1-2-3-4-1 cycle in Fig. 9, used in the CAN theory, represented by two isotherms 1-2 and 3-4 and two isentropic 2-3 and 4-1. The cycle receives the heat flow \dot{q}_w from the warm source of temperature $T_{ep,s} = \text{const}$, yields the heat flow \dot{q}_s to the sink source of temperature $T_{ep,w} = \text{const}$, and produces the mechanical power \dot{w} . Following the interaction with the warm and sink sources, the working fluid reaches temperatures $T_{f,w} = \text{const} \leq T_{ep,w}$, respectively, $T_{f,s} = \text{const} \geq T_{ep,s}$ by non-coupled transfer of the convective type. The CAN theory aims at the maximization of the power of cycle 1-2-3-4-1, which is considered endoreversible, by equation

$$\frac{\dot{q}_w}{T_w} + \frac{\dot{q}_s}{T_s} = 0 \quad (64)$$

In Eq. (64), obtained by the integration and derivation of Eq. (62) in relation to time, the heat flows \dot{q}_w and \dot{q}_s are assessed by means of Eq. (54). The calculation is made together with the power balance equation

$$\dot{q}_w + \dot{q}_s = \dot{w} \quad (65)$$

The cycle delivers maximum power when $T_{f,s}$ and $T_{f,w}$ have the optimal ratio [13]

$$\frac{T_{f,s}}{T_{f,w}} = \sqrt{\frac{T_{ep,s}}{T_{ep,w}}} \quad (66)$$

In the phenomenological theory, Eq. (64) is replaced by the stationary Eq. (46). Hereinafter it will be demonstrated that it is in fact a Clausius integral, at least in the case of the cycle under study. Indeed, the application of Eq. (46) to the cycle 1-2-3-4-1 leads to the following balance of natural forces

$$\begin{aligned} & \left[(-X)_{ncpl,2} - (-X)_{ncpl,1} \right] + (-X)_{ncpl,w,2-3} \\ & + \left[(-X)_{ncpl,4} - (-X)_{ncpl,3} \right] + (-X)_{ncpl,w,4-1} = 0 \end{aligned} \quad (67)$$

where, according to Eqs. (15), (17) and (18),

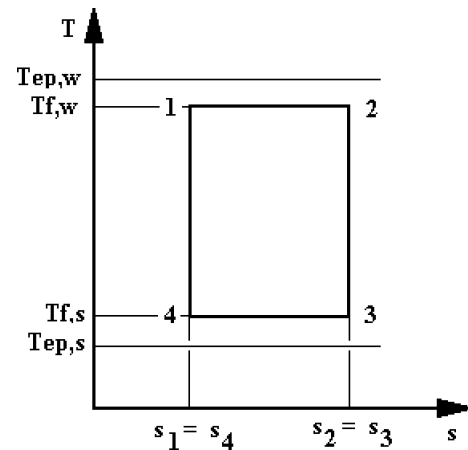


Fig. 9. The irreversible Carnot cycle connected to sources by non-coupled transfer and used in the phenomenological CAN theory assessment.

$$\begin{aligned} (-X)_{ncpl,1} &= - \left[(s_1 - s_{ep,w,1}) + h_{ep,w,1} \left(\frac{1}{T_1} - \frac{1}{T_{ep,w}} \right) \right] \\ (-X)_{ncpl,2} &= - \left[(s_2 - s_{ep,w,2}) + h_{ep,w,2} \left(\frac{1}{T_2} - \frac{1}{T_{ep,w}} \right) \right] \\ (-X)_{ncpl,w,2-3} &= - \left[\left(s_2 + \frac{h_2}{T_2} \right) - \left(s_3 + \frac{h_3}{T_3} \right) \right] \\ (-X)_{ncpl,3} &= - \left[(s_3 - s_{ep,s,3}) + h_{f,s,3} \left(\frac{1}{T_3} - \frac{1}{T_{ep,s}} \right) \right] \\ (-X)_{ncpl,4} &= - \left[(s_4 - s_{ep,s,4}) + h_{f,s,4} \left(\frac{1}{T_4} - \frac{1}{T_{ep,s}} \right) \right] \\ (-X)_{ncpl,w,4-1} &= - \left[\left(s_4 + \frac{h_4}{T_4} \right) - \left(s_1 + \frac{h_1}{T_1} \right) \right] \end{aligned} \quad (68)$$

Account is taken of the fact that

$$\begin{aligned} T_1 &= T_2 = T_{f,w} \\ T_3 &= T_4 = T_{f,s} \\ s_2 &= s_3 = s_{ep,w,2} = s_{ep,s,3} \\ s_1 &= s_4 = s_{ep,w,1} = s_{ep,s,4} \end{aligned} \quad (69)$$

and together with Eqs. (68), (67) becomes

$$\begin{aligned} & \frac{h_1 - h_2}{T_{f,w}} + \frac{h_3 - h_4}{T_{f,s}} + (h_{ep,w,2} - h_{ep,w,1}) \left(\frac{1}{T_{f,w}} - \frac{1}{T_{ep,w}} \right) \\ & + (h_{f,s,4} - h_{f,s,3}) \left(\frac{1}{T_{f,s}} - \frac{1}{T_{ep,s}} \right) = 0 \end{aligned} \quad (70)$$

The equation of the first principle of thermodynamics is written under the form

$$dq = dh - v dp \quad (71)$$

and is integrated between states 1 and 2, and then between states 3 and 4, obtaining

$$q_w = (h_2 - h_1) - \int_1^2 v dp \quad (72)$$

respectively,

$$q_s = (h_4 - h_3) - \int_3^4 v dp \quad (73)$$

Eqs. (72) and (73) are introduced in Eq. (71), obtaining

$$\frac{q_w}{T_{f,w}} + \frac{q_s}{T_{f,s}} = d_r \leq 0 \quad (74)$$

where quantity

$$\begin{aligned} d_r = & - \left(\frac{1}{T_{f,w}} \int_1^2 v dp + \frac{1}{T_{f,s}} \int_3^4 v dp \right) \\ & + (h_{ep,w,2} - h_{ep,w,1}) \left(\frac{1}{T_{f,w}} - \frac{1}{T_{ep,w}} \right) \\ & + (h_{f,s,4} - h_{f,s,3}) \left(\frac{1}{T_{f,s}} - \frac{1}{T_{ep,s}} \right) \leq 0 \end{aligned} \quad (75)$$

is referred to herein as *reversibility defect* (obviously, of the considered Carnot cycle). It is easy to demonstrate that the reversibility defect is zero only if, simultaneously, (i) the working fluid is an ideal gas, in which case the first term is annulled, and (ii) $T_{f,w} \rightarrow T_{ep,w}$ and $T_{f,s} \rightarrow T_{ep,s}$, in which case the last two terms are annulled. Obviously, in our case we have $d_r < 0$. Thus it has been demonstrated that Eq. (46), through Eq. (74), is the Clausius equation for the Carnot cycle 1-2-3-4-1, which is therefore irreversible. It further follows that, from the phenomenological point of view, endoreversibility is an unrealistic simplification, and the CAN theory based thereon, appears to be simplistic, and insufficiently substantiated. This theory weak point is emphasized in a good part of past works by others [17,18], but is still neglected in many other advanced studies [19, 20]. Parallel studies were also accomplished to optimize the power output of irreversible cycles for various scenarios of irreversibility (e.g., for the irreversible Carnot cycle [21]). The phenomenological approach of the problem at hand is hereinafter considered for a case study of the irreversible Carnot cycle shown in Fig. 9, which operates with CO₂ gas. For this application the set of input data mentioned in the explanatory notes to Fig. 9 was chosen at random. The power of the cycle was assessed by solving the algebraic system consisting of Eqs. (70) and (65), phenomenologically expressed by Eq. (76) below

$$\begin{aligned} & [h_{f,w,2}(-X)_{ncpl,2} - h_{f,w,1}(-X)_{ncpl,1}] \\ & + [h_{f,s,4}(-X)_{ncpl,4} - h_{f,s,3}(-X)_{ncpl,3}] + \frac{\dot{w}}{L} = 0 \end{aligned} \quad (76)$$

The phenomenological coefficients of pure non-coupled interactions are not available for this work and further theoretical studies are necessary to obtain them. However, in Eq. (76), for the sake of simplicity, we considered them as constant ($L = \text{const}$), without to change the main results of our presentation. The result of the calculation carried out by means of the same commercial code [15] is

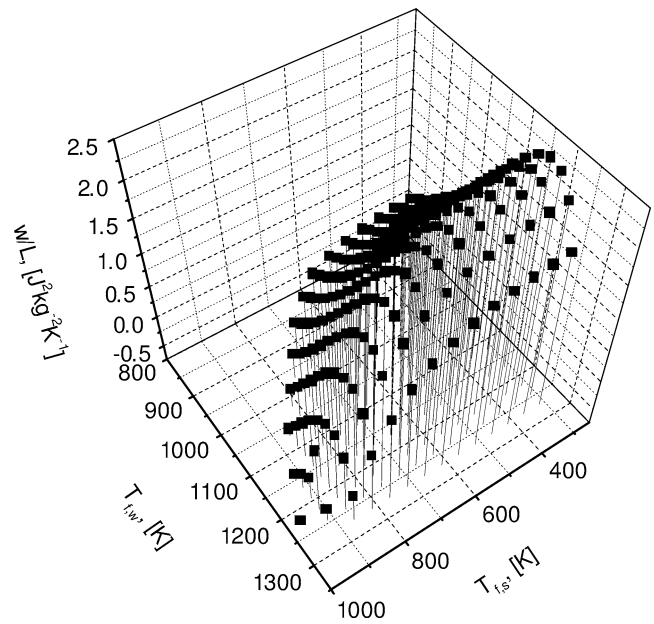


Fig. 10. Power diagram of the irreversible Carnot cycle against working fluid temperatures. Code inlet data: 1) Working fluid: CO₂ gas; 2) $T_{ep,w} = 1275$ K; $T_{ep,s} = 310$ K; 3) $s_1 = s_4 = s(t = T_{ep,w}, p = 240 \text{ bar}) = \text{const}$; $s_2 = s_3 = s(t = T_{ep,w}, p = 60 \text{ bar}) = \text{const}$.

presented in the chart shown in Fig. 10, for various values of temperatures $T_{f,s}$ and $T_{f,w}$, ranging from $T_{ep,s}$ and $T_{ep,w}$. The surface (\dot{w}/L) has a maximum value at the optimum temperatures $(T_{f,w})_{opt} \cong 1195$ K and $(T_{f,s})_{opt} \cong 315$ K, in agreement with the CAN theory, but the optimum values do not comply with Eq. (66). The optimum coordinates may be obtained directly, analytically, by searching for the extreme of the $(\dot{w}/L)(T_{f,s}, T_{f,w})$ function. This approach is extremely difficult and has been avoided even in the present case, which is one of the simplest. Although here the phenomenological methods and CAN differ from the value point of view, the fact that they are concordant from the point of view of the prediction of maximum power is encouraging. For this reason it should be assumed that a coupling of these two theories could be beneficial in a more realistic preliminary calculation of the optimization of the power cycle, heat pump, etc. To this effect, however, it will be necessary to conduct more thorough studies in future, which studies are beyond the framework of this paper.

6. Conclusions

The classic heat and mass transfer assessment bases on a “single-point” (equilibrium point) theory. According to this theory, the transfer is proportional to the system departure from the equilibrium point, what plays the role of a driving force. This paper continues the research initiated in some previous papers [1,2,7], presenting a non-equilibrium phenomenological theory of the mass and heat transfer, what could be characterized as a “two-point” theory (TPT). The paper introduces the notions of coupled, non-coupled and

mixed transfer and the two points what the theory bases on in the interactions of the system-source type: equilibrium and ideal. At the same time, the equations of the natural forces governing the coupled and non-coupled transfer in physical and chemical interactions are given. In its main part the paper shows the phenomenological coefficients of the mixed transfer and proves the basic theorems of the theory in the system-source interactions with non-coupled and mixed transfer (of the equilibrium point, of the existence and uniqueness of the ideal point and of maximization of the mixed transfer, respectively). Simple applications of water condensation/vaporization complete the theorems. To summarize, according to the TPT non-coupled mass and heat transfer is proportional to the departure from the equilibrium point, but the mixed transfer, unlike single-point theory, is maximized when the equilibrium point approaches the ideal point.

In the last part of the paper, the theory is applied to the analysis of the cyclic mass and heat transfer, pointing out the fact that, beside the mass conservation law and the first principle of thermodynamics, the cyclic mass and heat transfer is additionally subjected to the conservation of natural forces. This natural force property proves to be similar to Clausius integral, but additionally has the advantage of practical utility, enabling a direct easy use of the second principle of thermodynamics in the cyclic mass and heat transfer. TPT is first applied to a water cycle with mixed transfer of the heat pipe type. The results give for the first time a non-empirical explanation concerning the high heat transfer of a heat pipe observing that distances between the equilibrium points and the ideal points are quantified in such cycle at minimum values, specific to a maximum heat transfer according to the theorem of maximization of the mixed transfer. In a second application, a comparative TPT/CAN study concerning power output maximization of the irreversible Carnot cycle is effected, showing that, although endoreversibility is unrealistic, the two theories are essentially concordant and could be coupled in future in order to achieve a more realistic calculation of the cycles.

Appendix A

Using the vector additive property of the natural force, an isobaric interaction with a source (Eq. (15)) can be brought to a simpler form. In order to proof Eq. (16), it is enough to consider a system-source interaction. We shall start from an elementary interaction between $T' = T + dT$ si $T_{ep} = T$. With $n' = 1$, Eq. (15) leads to the elementary force

$$d(-X)_{ncpl,s,p} = \left[s(T + dT) - s(T) + h(T + dT) \left(\frac{1}{T + dT} - \frac{1}{T} \right) \right]_p \quad (A.1)$$

or, developing in Taylor series and keeping the linear form only, we obtain

$$d(-X)_{ncpl,s,p} = - \left(ds - \frac{h}{T^2} dT \right)_p \quad (A.2)$$

We take into account the equation of the first principle of thermodynamics for isobaric processes in Eq. (A.2)

$$ds = \left(\frac{dh}{T} \right)_p \quad (A.3)$$

where from the elementary force rewrites

$$d(-X)_{ncpl,s,p} = -d \left(\frac{h}{T} \right)_p \quad (A.4)$$

The force between two states, initial T' and final T_{ep} , is obtained integrating Eq. (A.4)

$$\begin{aligned} (-X)_{ncpl,s,p} &= - \int_{T_{ep}}^{T'} d \left(\frac{h}{T} \right)_p \\ &= - \left[\left(\frac{h}{T} \right)(T') - \left(\frac{h}{T} \right)(T_{ep}) \right] \end{aligned} \quad (A.5)$$

where the state thermodynamic function $(h/T) = s_t$ is termed here (*mass and heat*) *transfer entropy*.

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