

COMPARISON BETWEEN THERMAL MACHINES AND FUEL CELL TREATMENT IN THE FRAMEWORK OF THERMODYNAMICS WITH FINITE SPEED

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Abstract. The main Moments in the Historical Development of Thermodynamics with Finite Speed (TFS), the Essence of it, the New Parameters (Instantaneously average parameters of state) introduced for description of Finite Speed Processes, The main Formulas and Tools introduced and used in TFS, the main Method for Optimization of the Speed, Temperature and other parameters of irreversible cycles, called The Direct Method - with their Achievements and Validation are presented. The Essence of TFS is the combination of the First Law of Thermodynamics for Processes with Finite Speed with the Second Law of Thermodynamics. The Advantage of it (in comparison with the other branches of Irreversible Thermodynamics - IT) consists in the ability to obtain the performances of any cycle with Finite Speed (Efficiency/ COP and Power) by taking into account from the start, both internal and external irreversibilities. How this new branch of IT could help improve the Design of Thermal Machines and Relations with the other branches of Irreversible Thermodynamics and the Tendency of Unification, are presented in the second part of the paper. The analogy between the quantitative treatment of irreversible processes in Thermal Machines (TM) and those in Electrochemical Devices (ED: Fuel Cells, Electrolysers and Batteries) is discussed. This analogy is based on expressing the First Law of Thermodynamics for irreversible processes with Finite Speed, combined with the Second Law, in a similar format in both fields (TM and ED). From a methodological point of view, this treatment becomes the starting point for a unitary approach of **Thermodynamics with Finite Speed** (TFS) in the two domains historical independently developed: Engineering Thermodynamics and Electrochemistry. This analogy and the similar quantitatively treatment shows in fact, that all irreversibilities (either in TM or in ED) are generated by their Finite Speed.

Key Words: thermodynamics with finite speed, internal and external irreversibilities, First Law for processes with finite speed combined with the Second Law, irreversible cycles with finite speed, the direct method, irreversible processes in fuel cells, irreversible performances

Rezumat: Lucrarea prezintă momentele importante din Dezvoltarea Termodinamicii cu Viteză Finită (TVF), esența acesteia, noii parametri (parametrii de stare instantanei și medii) introduși pentru descrierea proceselor cu viteză finită, principalele formule și instrumente de calcul introduse și folosite în TVF, metoda principală de Optimizare a vitezei, temperaturii și a altor parametri ai ciclurilor ireversibile, numită Metoda Directă - cu realizările obținute până la Validare. Explicarea matematică a Primului Principiu al Termodinamicii pentru Procese cu Viteză Finită combinat cu cel de al doilea Principiu este esența TVF. Avantajul ei (în comparație cu alte ramuri ale Termodinamicii Ireversibile - TI) constă în capacitatea de a obține performanțele oricărui ciclu cu viteză finită (Randamentul / COP și Puterea Produsă / Consumată) deoarece ia în considerare chiar din start, ambele tipuri de pierderi: interne și externe. Cum poate ajuta această nouă ramură a TI în Proiectarea Optimizată a Mașinilor Termice, relațiile TVF cu alte ramuri ale TI, precum și tendințele de unificare între diversele ramuri ale Termodinamicii Ireversibile sunt prezentate în partea a doua a lucrării.

Este prezentată analogia dintre tratarea cantitativă a proceselor ireversibile în Mașinile Termice (MT) și Dispozitivele Electrochimice (DE: pile de combustie, electrolizoare și baterii). Această analogie se bazează pe expresia Primului Principiu al Termodinamicii pentru Procese cu Viteză Finită combinat cu cel de al doilea Principiu, tratată în același format în ambele domenii (MT și DE). Din punct de vedere metodologic, această tratare constituie punctul de plecare al abordării unitare a Termodinamicii cu Viteză Finită (TVF) în cele două domenii, Termodinamica Inginerească și Eletrochimia, care, istoric, s-au dezvoltat independent. Această analogie și tratarea cantitativă similară arată, de fapt, că toate ireversibilitățile (fie din MT, fie din DE) sunt generate de Viteza Finită de desfășurare a proceselor implicate.

Cuvinte Cheie: termodinamica cu viteză finită, ireversibilități interne și externe, primul principiu combinat cu principiul al doilea pentru procese cu viteză finită, cicluri ireversibile cu viteză finită, Metoda Directă, procese ireversibile în pile de combustie, performanțe.

1. INTRODUCTION

A correct comparison between Performances of Fuel Cells and Thermal Machines should be based on comparing *the same kind of processes* regarding their *reversibility (ideal operation) or irreversibility (real operation)*.

This means that we have to always compare either the reversible Efficiencies of them on one side, or the irreversible (real) Efficiencies, on the other side. Consequently, by no means we can compare reversible Efficiencies with irreversible Efficiencies, because such a “comparison” does not make any sense.

Also note that despite the fact that Fuel Cells do not use a thermodynamic cycle as the Thermal Machines do, in order to transform a form of energy into another, both will follow the Second Law of Thermodynamics.

In this paper we further investigate the differences and similarities of applying the Second Law for Fuel Cells and Thermal Machines in order to compute their Performances, Efficiency and Power, using the recent achievements of Thermodynamics with Finite Speed (TFS) [1-58]. In this relatively new branch of what we can generally call Irreversible Thermodynamics (all the branches dealing with irreversible processes using different methods), new concepts and new equations have been introduced in order to take into account quantitatively the irreversibilities in real Thermal Machines, where processes develop with Finite Speed. It was shown that the main causes of irreversibilities (internal and external) depend on the same real operation parameter, which is the Finite Speed of the Piston w_p . In Fuel Cells, because the conversion of chemical energy in electricity is directly made, without using a cycle and a system of the cylinder-piston type, we cannot talk about the “speed of the piston”. Because of that, at a first glance, it would be difficult to find similarities between the operation of real Fuel Cells and real Thermal Machines. Despite these difficulties, we have discovered [20]-[22], [28], [25], [64] that very important similarities exist between the operation of real Fuel Cells and real Thermal Machines, regarding the fact that both work with internal irreversibilities, in addition to the external ones, and these irreversibilities decrease the performances (Efficiency and Power) in comparison with the reversible ones. In Thermal Machines, along with the increase of the piston speed, these performances decrease as well.

A similar fact is happening in Fuel Cells, a well-known fact by electrochemists, namely that

with the increase of the *current density* $i=I/A$ (*Intensity of the current/Area of the electrodes*) also the performances will decrease. We will show in this paper that the analogy of the role of *piston speed* and the *current density* as main causes of *internal irreversibilities* is based on the real fact that any irreversible process with “finite speed”, respecting the *second part of the Second Law* will conduct not only to decrease of Performances (*Efficiency and Power*) but will also have similar equations, from a mathematical point of view. This fact is by no means just “a coincidence”. It is based on the *similar physical origins of the molecular mechanisms of generating irreversibility when the processes take place with “finite speed”*. This similarity is expressed in the same mathematical form of the *First Law of Thermodynamics (combined with the Second Law) for any kind of irreversible process, either expansion/compression in the piston cylinder system (Thermal Machine) or in the charging/discharging an electrochemical device*. The final result of this analogy will be reflected in *the same mathematical format of irreversible efficiencies*:

$$\eta_{irr} = \eta_{rev} \cdot \eta_{II}(\text{Finite Speed}) \quad (1)$$

where:

η_{irr} = Irreversible Efficiency of the Fuel Cell (or any ED) or of the TM,

η_{rev} = Reversible Efficiency of the Fuel Cell (or any ED) or of the TM,

η_{II} (Finite Speed) = Second Law Efficiency as function of the “finite speed” of the process, which will be: $i = \text{density of the current}$ for Fuel Cells, and

$w_p = \text{speed of the piston}$, for Thermal Machines.

This analogy (similarity) goes further, namely the Second Law Efficiency, η_{II} has the same mathematical structure/format in both cases, the only difference being that in the first case i intervenes, and in the second case w_p intervenes [66, 28, 23, 53, 24, 25, 64]:

$$\eta_{II} = [1 \pm \Sigma(\text{Finite Speed of macroscopic process} / \text{Finite Speed of microscopic interaction})] \quad (2)$$

where:

Finite Speed of microscopic process = i (for Electrochemical Devices) or w_p (for Thermal Machines);

Finite Speed of interaction = i_o (exchange current for ED) or c (average molecular speed for TM);

(\pm) is a *new sign*, which will be (+) for the *processes in which energy is introduced* in the system: *charging* (for ED) or *compression* (for TM) and (-) for processes in which energy “is produced” by the system is obtained from the

system as *mechanical work*, expansion for TM, or *electrical work*, discharge for ED.

In this way, Thermodynamics with Finite Speed (TFS) offer a “unified view” of the quantitative and qualitative treatment of irreversible processes in the domains of Thermal Machines and Electrochemical Devices, based on the First Law and Second Law of Thermodynamics, emphasizing that the *origin of irreversibility in all real processes* is the same, namely the *Finite Speed of the processes either macroscopic or microscopic*. Based on the same mathematical treatment, the *Sensitivity Studies for Fuel Cells and Thermal Machines and Optimization of Design* are made in a similar way or with similar methods. In both domains we are looking for *Optimum Speed (i or w_p)* corresponding either to *Maximum Efficiency* or to *Maximum Power*.

2. THE DEVELOPMENT OF THERMODYNAMICS WITH FINITE SPEED AND THE DIRECT METHOD

In 1937 a German physicist M. Paul [1] studied the first *Process with Finite Speed* in a piston cylinder arrangement, and obtained the first equation of an *adiabatically irreversible Process with Finite Speed*:

$$TV^{(k-1) \cdot (1 \pm 2.60067 w/c + 3 w^2/c^2 \pm 3.6743 w^3/c^3)} = \text{Const} \quad (3)$$

where: w - is the *Piston Speed*, and $c = (3RT)^{1/2}$, is the *Average Molecular Speed* (Clausius formula).

Much later (1964), and independent of this discovery, but inspired from the books of W. Macke [2], A. Sommerfeld [3], and Einstein's Theory of Relativity [4,8], S. Petrescu working for his Ph.D Thesis [10], with his adviser Prof. L. Stoicescu [9] has written for the first time a new equation for the *First Law of Thermodynamics for Processes with Finite Speed* in closed systems (Piston - Cylinder arrangement):

$$dU = \delta Q - P_{m,i} \cdot (1 \pm aw/c) \cdot dV \quad (4)$$

This approach [9], [10] of *Irreversible Processes with Finite Speed* was completely new and different in comparison with Paul's approach [1]. Paul was not interested to find a new equation for the *First Law of irreversible processes*, like Eq. (4), but just to get an equation of *irreversible adiabatic process with Finite Speed*, Eq. (3).

Getting the Eq. (4), in 1964 [9, 10] can be considered the beginning of **Thermodynamics with Finite Speed**, because *for the first time the causes for irreversibility were contained in a fundamental equation of Thermodynamics*, namely in the Mathematical Expression of the First

Law, written especially for irreversible processes, in an explicit way, as function of the **Finite Speed of the Piston w** , and **Finite Speed of the Molecules c** . The analogy with Einstein's Theory of Relativity [4,8], consists in the fact that in a similar way like the electromagnetic waves interaction depends on the speed of light, here in the piston cylinder arrangement, the waves generated by the motion of the *piston with finite speed w* , depend on the *average molecular speed c* . Because of that, the **mechanical interaction** between Piston and the Gas, (which is **irreversible elementary Work δW_{ir}**) must depend on the ratio w/c , was the seminal idea [8], which conducted us to the equation (4), using 4 different approaches:

a) **The basic kinetic-molecular model** [9], [10] led to the following relationship:

$$\delta W_{irr} = P_{m,i} \cdot \left[1 \pm \frac{aw}{c} + \frac{bw^2}{c^2} \pm \dots \right] \cdot dV = P_p \cdot dV ;$$

$$a = 2; b = 5; c = \sqrt{3RT_{m,i}} \quad (5)$$

b) **The advanced kinetic-molecular model** [10, 16], based on Maxwell-Boltzmann distribution and on *finite relaxation time* in the system led to:

$$\delta W_{irr} = P_{m,i} \cdot \left[1 \pm 2,764 \frac{w}{c} + 3 \frac{w^2}{c^2} \pm 1,283 \frac{w^3}{c^3} + \dots \right] \cdot dV$$

$$(6)$$

c) **The phenomenological analysis based on the propagation of pressure waves, generated by the finite speed of the piston and the speed of sound in the gas** [9], [10] led to:

$$\delta W_{irr} = P_{m,i} \cdot \left[1 \pm \frac{aw}{c} \right] \cdot dV ; a = \sqrt{3k} ; k = C_p/C_v ;$$

$$c = \sqrt{3RT_{m,i}} \quad (7)$$

d) **The Second Law Treatment** [19], based on the **Linear Irreversible Phenomenological Thermodynamics of Onsager** [6] and **Prigogine (LIPT)** [7], and the concept of **Entropy Generation**, led to:

$$\delta W_{irr} = P_{m,i} \cdot [1 \pm K_1 \cdot w] \cdot dV \quad (8)$$

Where: K_1 is a constant which depends on the properties and *instantaneous mean temperature* of the gas.

The second term in the right member of Eq (4) is the irreversible work δW_{ir} :

$$\delta W_{ir} = P_{m,i} \cdot (1 \pm aw/c) \cdot dV \quad (9)$$

Here we have again introduced something completely new in comparison with Reversible

Thermodynamics, namely the parameter $P_{m,i}$ which is called - **instantaneously mean pressure in the system**, which is different compared with the **pressure on the piston P_p** (which produces or consumes work in the interaction between the system and the surroundings):

$$P_p = P_{m,i} \cdot (1 \pm w/c) \tag{10}$$

Because the two pressures are different when the *Piston Speed* w is greater than zero, and c

smaller than infinity (infinite temperature), it was necessary to introduce two curves in the P - V diagram, thus becoming capable of describing such *irreversible processes with Finite Speed w* (Fig. 1 and Fig. 2). **The whole development of Finite Sped Thermodynamics is based on the Eq. (4) together with all these new concepts, without which these irreversible processes cannot be described.**

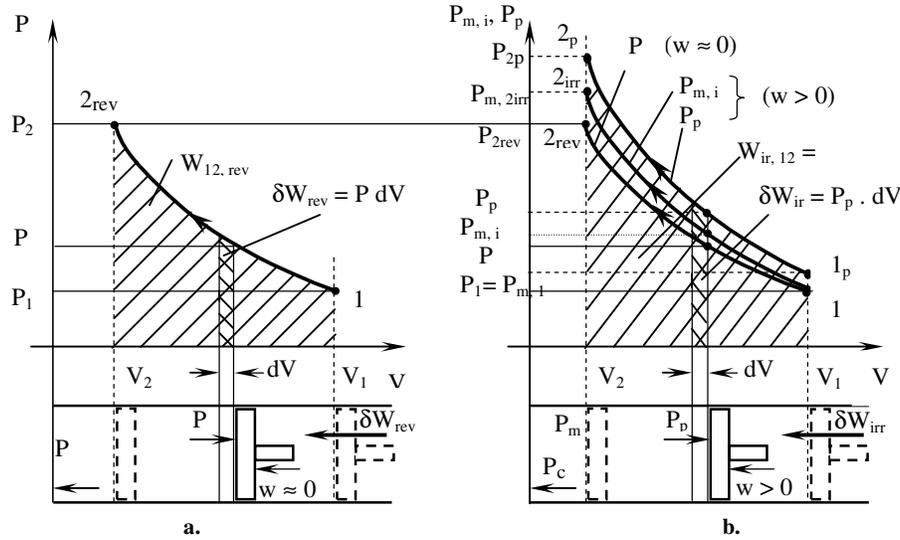


Fig. 1. Comparison between P-V diagrams for reversible (a) compression ($w \approx 0$) and irreversible (b) compression ($w > 0$)

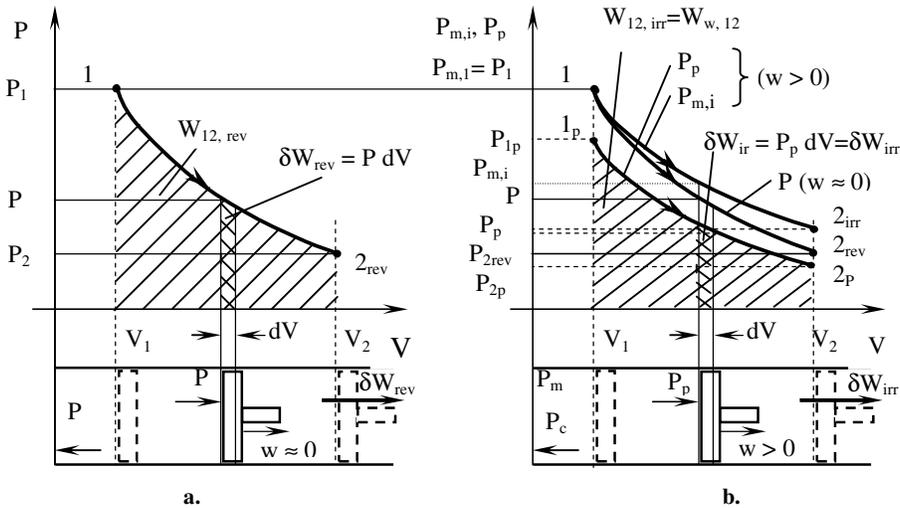


Fig. 2. Comparison between P-V diagrams for reversible (a) expansion ($w \approx 0$) and irreversible (b) expansion ($w > 0$)

3. IRREVERSIBLE CYCLES WITH FINITE SPEED IN THERMAL MACHINES

Based on Eq. (4) L. Stoicescu and S. Petrescu have done in 1965 the first study of an **Irreversible Cycle with Finite Speed** for the case of **Otto Irreversible Cycle with Finite Speed** [10], [13]. The title of this paper was essential for the

Development of TFS, namely: “**Thermodynamic Cycles with Finite Speed**” [13]. In this paper [10], an analytical expression for the **Efficiency of Otto irreversible cycle with finite speed**, was obtained for the first time. All these developments and also others that followed were based on eq. (2). This was the main difference between Paul’s approach (studying just one irreversible process) and the

fundamental approach, of “all the irreversible processes” based on the same *Fundamental Equation* (4), which *in fact combine the two main Laws of Thermodynamics* (First and Second Law). Building a “New Thermodynamics”, namely *Irreversible Thermodynamics for Processes with Finite Speed* (TFS) was the goal of Petrescu’s Ph.D Thesis [10]. This was done in the above papers and several others which followed between 1964-1992, only taking into account *one cause of irreversibility* (the term *aw/c*). Much later in 1992-1994 the other two causes of irreversibility, *friction and throttling*, were taken into account [23]-[25], [42]. Based on those papers [23]-[25] a more intensive Development of Thermodynamics with Finite Speed conducted to the formulation of the **Direct Method** [24]- [29] and its applications: [29]-[53]. It is important to remark that, historically speaking, the paper [9] from TFS was published 10 years before Curzon – Ahlborn seminal paper regarding *Thermodynamics with Finite Time* [30]. It is a well-known fact that this paper [30] opened the “explosive *development*” of the *Thermodynamics with Finite Time* (TFT) which did not take into account internal irreversibilities, but only external irreversibilities, generated by temperature gradient between the System and the Heat Sources. The cycles studied by this early TFT [30]-[32] were called **endoreversible**. This is the essential difference between the origin of TFS [9]-[19] and the origin of TFT [30]. Namely TFS, from the very beginning takes into account both irreversibilities: internal and external, but TFT takes into account only the external ones (for endoreversible cycles).

Much later, starting with Ibrahim [49] in 1991, more and more researchers also started to take into account the internal irreversibilities in their papers regarding *Thermodynamics with Finite Time*.

A comparison between TFT and TFS approach has been made by us in the paper [52]. In TFT the accent is put on the optimization of time and temperature usually taking into account only external irreversibilities. In TFS the accent is put on the optimization of the speed and temperature, but taking into account both irreversibilities (internal and external).

Of course the optimization result is different, and TFS gives more realistic results for Thermal Machines. The proof is that **TFS was Validated** [53] and TFT cannot, as it does not take into account internal irreversibilities. In the last years some papers from TFT took into account some of internal irreversibilities.

4. WHAT IS THE DIRECT METHOD AND WHAT CAN BE DONE WITH IT?

The **Direct Method** consists in the study and evaluation of irreversibilities of real thermal machines by analyzing the cycle step by step and by **direct integration** of the equation of the First Law combined with the Second Law for processes with Finite Speed [9], [10], [23], [24] for each process in the cycle. In this way we can obtain **direct analytical expressions for the Efficiency (or COP) and Power as function of the speed of the process and other geometrical or functional parameters of the cycle.**

This Direct Method has been used in order to study classical Stirling Engines [34], [41], [45], [50],[53], Solar Stirling Motors [54], [56], [57], Stirling Refrigeration and Stirling Heat Pumps [25], Otto cycle [46], Diesel Cycle [47], Carnot Cycle [29], [33], [44], [51], [52], Refrigeration Cycle [44], Otto-Stirling Hybrid cycle [55], [58], [58] and Brayton cycle. For 12 of the most performing Stirling Engines (working in 16 regimes of functioning) [53], for 4 (the most performing) Solar Stirling Motors [54], [56], [57] and for a Refrigeration Stirling Machine [68] we have validated the developed schemes of computation based on the Direct Method. This is a proof that the Direct Method is a powerful tool in the Optimization and Design of thermal machines, based on Thermodynamics with Finite Speed, which become a useful Irreversible Thermodynamics Branch for engineers.

In 1992, S. Petrescu et.al [23] has generalized Eq. (2) for Complex Systems, which contains three causes of irreversibility, namely *Finite Speed, Throttling and Friction*:

$$dU = \delta Q_{ir} - P_{m,i} \cdot (1 \pm aw/c \pm b \cdot \Delta P_{th}/2P_{m,i} \pm f \cdot \Delta P_f/P_{m,i}) \cdot dV \quad (11)$$

The generalization of the work equation from TFS-for Simple Systems (5) to Complex Systems conducted to the following expression [23, 24, 66, 64 and 25]:

$$\delta W_{ir} = P_{m,i} \cdot (1 \pm aw/c \pm b \cdot \Delta P_{th}/2P_{m,i} \pm \Delta P_f/P_{m,i}) \cdot dV \quad (12)$$

More Complex Systems will closer model the real Thermal Machines operation, using the above equation. Despite of the similarity of Eq. (17) from TFS-for Complex Systems and Eq. (2) from TFS-for Simple Systems, there is a very important and subtle difference between them. Namely, the second term in the right part of Eq. (17) is not the irreversible work, which is the case of Eq. (2) and

also the case of Equation of the First Law from Reversible Thermodynamics (RT):

$$dU = \delta Q - P.dV \quad (13)$$

Namely, in Eq. (12) there is no f as it is in Eq. (11), which describe the process, where f intervenes in the second term. That second term is **not the work**, as it is in the case of Eq. (13) from RT, because it also contains the contribution of friction work transformed in heat and accumulated into the system. Because of this important aspect we have to use, in TFS-for Complex systems, two Eq., (11) and (12), in order to describe the process with Eq. (11) and also to compute the work, Power and also the Efficiency of the irreversible cycle with finite speed with Eq. (12).

This Eq. (11) together with Eq. (12) becomes The **Fundamental Equations of Irreversible Processes with Finite Speed for Complex Systems**, which contains all three causes of irreversibility. The moment 1992 [23] can be considered the **beginning of the Development of Thermodynamics with Finite Speed for Complex Systems** and the essential fact about it is that Eq. (11) and (12) combined with new **PV/Px Diagrams led us to the Validation of the Schemes of Optimization of Stirling Machines based on the Direct Method [53]**. Because of that, it can be used for real Optimization of Thermal Machines, which was not the case of Thermodynamics with Finite Time. Exactly for this reason some important critics were expressed about TFT by Giftopoulos [37] and Moran [38], [39]. These critics cannot be made for TFS, because, based on Eq. (11) and (12) together with the Direct Method, TFS can contribute effectively to the Design and Efficient Optimization of Thermal Machines, which is exactly what engineers expected from a **new Branch of Irreversible Thermodynamics**.

We can be confident that TFS could satisfy the expectations of engineers around the world involved in getting better and better Designs, meaning higher Efficiency and/or higher Power. For classical cycles the two maximum are not achieved at the same speed, but for Solar Engines the two maximum are achieved for the same speed [35, 44, 57, 54].

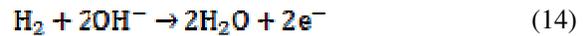
5. FIRST LAW OF THERMODYNAMICS COMBINED WITH SECOND LAW FOR FINITE SPEED PROCESSES IN ELECTROCHEMICAL SYSTEMS: FUEL CELLS, ELECTROLYZERS AND BATTERIES

Seminal papers regarding irreversible processes in thermal Machines [9]-[19] were followed by studies of **Irreversible Processes in Electrochemical Systems** by V. Petrescu, S. Petrescu, S. Sternberg et. al. [20]-[22]. These studies resulted in the **generalization of the First Law of Thermodynamics for Finite Speed Processes for Electrochemical devices (ED) such as Fuel Cells, Electrolyzers and Batteries**. [66, 28, 25, 64] Ultimately, this led to a **Unified approach of Thermal Machines and Electrochemical Devices using a unique method, called the Direct Method [27], [28]**. This method is based on the fact that the **First Law of Thermodynamics for Finite Speed Processes has the same mathematical format for both Thermal Machines and Electrochemical Devices, in the case of Irreversible Processes**.

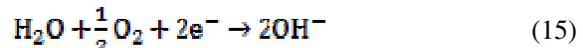
5.1. Reversible Performances in Hydrogen – Oxygen Fuel Cell [33].

In a H₂/O₂ Fuel Cell electrical power P_e is produced by means of “controlled” chemical reactions which take place in the porous *anode* and *cathode* (Fig. 3). In this Fuel Cell pure Hydrogen and Oxygen are continuously added to the cell producing water and electricity.

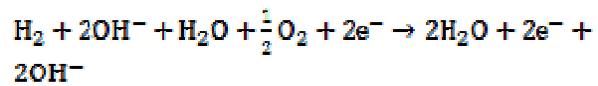
The chemical reaction at the *anode* is:



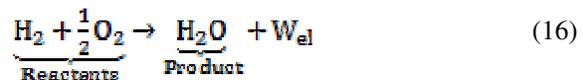
and at the *cathode*:



By the addition of equations (14) and (15), we get the full chemical reaction in the fuel cell:



, or:



The maximum work can be calculated from the First and Second Law of Thermodynamics for reversible processes (for electrical current $I \rightarrow 0$), as follows:

$$(Ist) \quad dU = \delta Q_{rev} - pdV - \delta W_{el} \quad (17)$$

$$(IInd) \quad \delta Q_{rev} = TdS \quad (18)$$

With eq. (18) in (17) we get:

$$dU - TdS + pdV = -\delta W_{el} \quad (19)$$

For a reaction at constant temperature T and constant pressure p we get:

$$d(U + pV - TS) = -\delta W_{el} \quad (20)$$

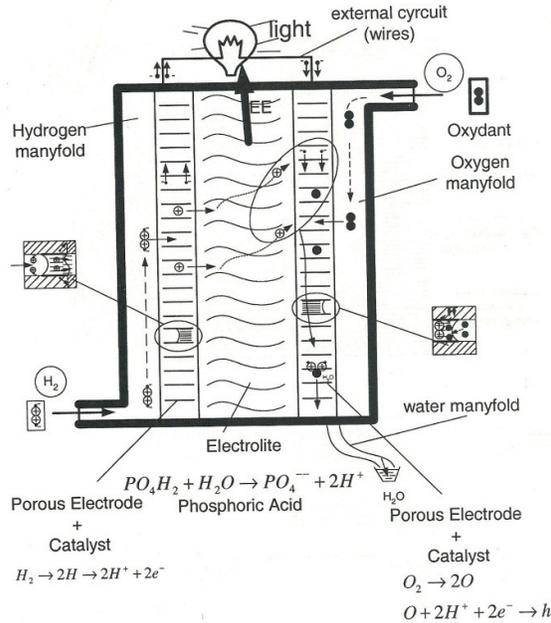


Fig 3. Hydrogen-Oxygen Fuel Cell

Integrating this equation (7) for a finite process between state 1 and 2:

$$\int_1^2 dG = \int_1^2 -\delta W_{el} \quad (21)$$

$$\text{or } \Delta G = -W_{el} \quad (22)$$

Where: the Variation of Gibbs Free Enthalpy ΔG can be calculated from the equation:

$$\Delta G = \sum_{\text{products}} \Delta G_{FP}^0 - \sum_{\text{reactants}} \Delta G_{FR}^0 \quad (23)$$

Where: ΔG_F^0 represents the Gibbs Free Enthalpy (or Gibbs Potential) required to form the particular molecule from the elements.

$$\Delta G = \sum \Delta G_{F,H_2O}^0 - \sum \Delta G_{F,H_2}^0 - \sum \Delta G_{F,O_2}^0 = -237100 - 0 - 0 - -237100 \text{ kJ/kmol} \quad (24)$$

Since the molecular mass of water is 18 kg/kmol, one can compute the variation of G per kg of H_2O produced:

$$\Delta G' = \frac{\Delta G}{M_{H_2O}} = -\frac{237100}{18} = -13177 \frac{\text{kJ}}{\text{kg}} H_2O \quad (25)$$

Finally, from (22) we get:

$$W_{\text{fuel cell max.}} = 13177 \frac{\text{kJ}}{\text{kg}} \quad (26)$$

The work done to convey the electrons from the cathode to the anode is also equal to nFV^0 (Faraday Law), where n represents the gram-moles of electrons, F is the Faraday constant

$$F = 96500 \text{ C/g} \cdot \text{mol} \quad (27)$$

and V^0 is the electrical potential across the anode and cathode when the circuit is open, that is when the external electrical resistance R_e is disconnected. Then we have:

$$V^0 = -\frac{\Delta G}{nF} \quad (\text{Open Circuit Voltage}) \quad (28)$$

5.2. Irreversible Performances of a real Fuel Cell operating with a finite current I and having an internal Resistance R_i

All real Fuel Cells working with “finite speed”, expressed by the finite electrical current intensity I , have 3 irreversibilities generated by 3 polarizations: Activation, Ohmic and Concentration polarizations. All of these will contribute to the decrease of the external voltage V of the Fuel Cells and to the increase of the “speed” of the process, actually measured by i .

Ohmic polarization is simple to understand, because it represent the decrease of voltage caused by the conversion of electrical energy into heat (Joule effect), when electricity is passing through an electrical internal cell resistance (of the electrolyte) R_i . Because this sort of irreversibility is the simplest one to understand, we present here the simplified case in which the two irreversibilities generated by the two polarizations, Activation and Concentration, are neglected. In the next paragraph all the 3 irreversibilities will be taken into consideration.

When the circuit is closed and an electrical current I is passing through an external resistance R_e (of the bulb - Fig.3.), the actual output voltage V is:

$$V = V^0 - IR_i \quad (29)$$

The electrical power P_e obtained from the Fuel Cell which is used for lighting a bulb (Fig.3) having the external resistance R_e , where finally the chemical energy of the fuel H_2 is converted into light and heat, is:

$$P_e = V \cdot I = R_e \cdot I^2 \quad (30)$$

where Ohm’s Law is used:

$$V = R_e I \quad (31)$$

In Fig.4 the external Voltage V is decreasing with the increase of external electrical current I , because of Ohmic polarization $I \cdot R_i$. On the other side, because of this the electrical Power P_e first increases, attains a maximum $P_{max} = 6.3 \text{ W}$ and after that decreases to zero. When the Power reaches maximum, this corresponds to an Optimum Intensity of the Current I_{opt} .

5.3. An analogy between the irreversibility in an electrochemical system (battery or fuel cell) and irreversibility in a mechanical system (a gas in a cylinder-piston system) [2,31]

The reversible work of a electrochemical cell is:

$$W_{rev} = -\Delta G = (OCV) \cdot n \cdot F \quad (32)$$

Reversible open circuit voltage (OCV) is:

$$(OCV)_{rev} = \frac{-\Delta G}{n \cdot F} = V^o \quad (33)$$

Irreversible Voltage $V_{D,irrev}$ in a discharge process (conversion of Gibbs Potential in electrical work) is:

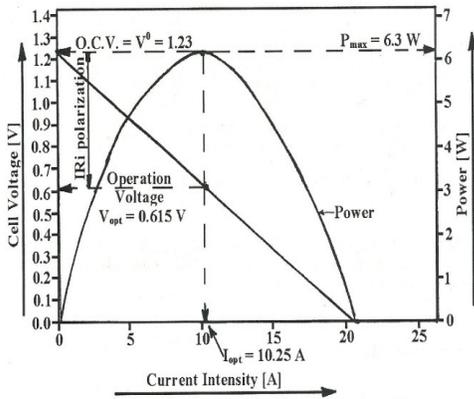


Fig. 4. Voltage – Current Intensity and Power curves for Hydrogen – Oxygen Fuel Cell

$$V_{D,irrev} = (OCV)_{rev} - I \cdot \sum R_{int,cell} - \eta_{ca} - \eta_{cc} - \eta_{aa} - \eta_{ac} \quad (34)$$

Irreversible work W_{irrev} in a discharge process will be:

$$W_{irrev} = V_{D,irrev} \cdot n \cdot F = (OCV)_{rev} \cdot n \cdot F \cdot \left[1 - \frac{I \cdot \sum R_{int,cell}}{(OCV)_{rev}} - \frac{\sum \eta_i}{(OCV)_{rev}} \right] \quad (35)$$

For activation polarization values less than RT/nF

$$\eta_a = \frac{RT}{nF} \cdot \frac{i}{i_0} \quad (i_0 = \text{exchange current}) \quad (36)$$

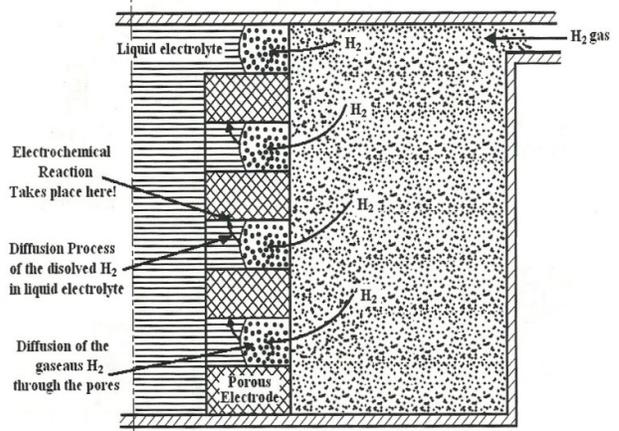


Fig. 5. "Half of the Fuel Cell". The origin of concentration overpotential (diffusion).

The concentration polarization can be expressed as function of the ratio between “two speeds”, namely the density of the current i and limiting current i_L , as follows:

$$\eta_c = \frac{RT}{nF} \cdot \ln \frac{i_L}{i_L - i} = \frac{RT}{nF} \cdot \ln \frac{1}{1 - \frac{i}{i_L}} \approx \frac{RT}{nF} \ln \left(1 + \frac{i}{i_L} \right) \quad (37)$$

$$\text{If: } i < i_L, \quad \eta_c \approx \frac{RT}{nF} \cdot \frac{i}{i_L} \quad (38)$$

With (36) and (38) in (35) W_{irrev} becomes:

$$W_{irrev} = \left[1 \mp \frac{I \cdot \sum R_{int}}{(OCV)_{rev}} \mp \frac{RT}{(OCV)_{rev} \cdot n \cdot F} \left(\frac{i}{i_{L,a}} + \frac{i}{i_{L,c}} \right) \mp \frac{RT}{(OCV)_{rev} \cdot n \cdot F} \left(\frac{i}{i_{O,a}} + \frac{i}{i_{O,c}} \right) \right] \cdot W_{rev} \quad (39)$$

With the signs: (-) for the discharging process, (+) for the charging process

The equation (39) is similar to that corresponding for irreversible work in a process of compressing or expanding a gas in a cylinder, with finite speed of the piston, with friction of the gas (throttling) and with friction between piston and cylinder.

$$\delta W_{irrev} = P_{average} \left(1 \mp \frac{a \cdot w}{c} \mp \frac{b \cdot \Delta P_g}{2 \cdot P_{average}} \mp \frac{\Delta P_f}{P_{average}} \right) \cdot dV \quad (40)$$

But $\delta W_{rev} = P \cdot dV$, so:

$$\delta W_{rev} = \left(1 \mp \frac{\Delta P_f}{P_{average}} \mp \frac{b \cdot \Delta P_{thr}}{2 \cdot P_{average}} \mp \frac{a \cdot w}{c} \right) \cdot \delta W_{rev} \quad (41)$$

With the signs: (-) for *expansion*; (+) for *compression*

The analogy between eq. (41) and eq. (39) is quite obvious. This analogy has two aspects:

The sign in parenthesis is changed if the energy is introduced in the system (*compression* in TM or *charging* in ED) or is extracted from the system (*expansion* in TM or *discharging* in ED).

Every term from parenthesis (39) and (41) has a correspondent:

-The term $\frac{I \sum R_{int}}{(OCV)_{rev}}$ which reflects the irreversibility generated by the "friction" of the electrons in the time of their motion thru internal resistors $\sum R_{int}$, has a correspondent in the term $\frac{\Delta P_f}{P_{average}}$ which takes into account the friction between the piston and the cylinder.

-The term $\frac{RT}{(OCV)_{rev} n F} \left(\frac{i}{i_{L,a}} + \frac{i}{i_{L,c}} \right)$ which reflects the irreversibility generated by the process of diffusion of ions, which moves towards the electrons in the electric field, i has a correspondent in the term $\frac{D \cdot \Delta P_{thr}}{2 \cdot P_{average}}$ which takes into account the irreversibility generated by the movement of the molecules through internal tubes or porous material of a regenerator (throttling process), which requires a ΔP_{thr} .

-The term $\frac{RT}{(OCV)_{rev} n F} \left(\frac{i}{i_{O,a}} + \frac{i}{i_{O,c}} \right)$ which reflects the irreversibility generated by the electrode reactions with finite speed of the electrons (the *density of current* i - finite), has a correspondent in the term $\frac{z \cdot w}{c}$, which takes into account the irreversibility generated by the finite speed of the piston w (and also of the process).

The importance of this treatment and the discovery of the analogy we have just mentioned above, consists in the fact that *Electrochemical Devices* (ED) and *Thermal Machines* (TM) can be treated on the same fundamental basis and concepts, related to the First Law of Thermodynamics (combined with the Second Law) developed for processes with Finite Speed (i for ED or w for TM), or developed for processes with finite time.

6. THE EXPRESSIONS OF EFFICIENCY AND POWER

Based on eqs. (11) and (12) we have studied several cycles with finite speed and have shown that in all these cases (Carnot, Otto, Stirling cycles) the efficiency and the power have a similar format:

$$\eta_{th} = \eta_{rev} \eta_{Ib,irrev(a)} \eta_{II,irrev(b)} \eta_{III,irrev(c)} \tag{42}$$

where: η_{th} - *thermal efficiency* of a cycle;
 η_{rev} - *reversible efficiency* of a cycle;
 $\eta_{II,irrev(a,b,c)}$ - *irreversible efficiency* caused by different causes (or mechanisms) of irreversibilities (a,b,c).

This format has been suggested by Bejan in a famous book [36] and it is interesting to notice that this format is also valid for Fuel Cells.

$$\eta_{el} = \eta_{rev} \cdot \eta_{Ib,irrev} = \eta_{izot} \cdot \eta_{II,irrev} \tag{43}$$

where: η_{el} = *Electrical Efficiency* of the Fuel Cell or Battery;

$$\eta_{rev} = \eta_{izot} = \text{Reversible Efficiency} = \text{Isothermal Efficiency};$$

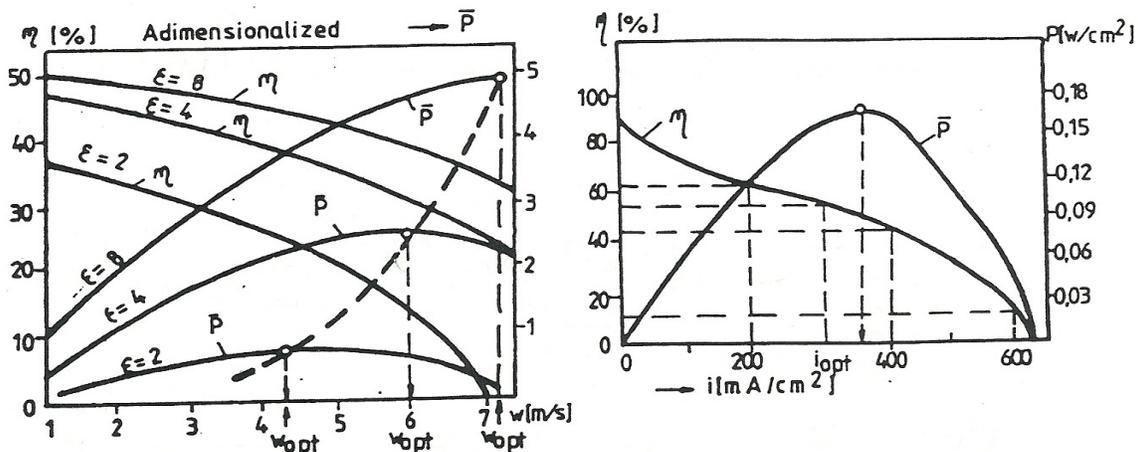


Fig. 7. Comparison between the *Efficiency* and *Power* curves for a Stirling Engine and a Fuel Cell.

$\eta_{II,irrev}$ = *irreversible efficiency* generated by the electrochemical processes with finite density current i .

$$\eta_{II,irrev,Fuel\ Cell} = (1 - \Sigma \eta_{pol}/E_{rev}) \quad (44)$$

$$\eta_{II,irrev,Battery} = (1 - \Sigma \eta_{pol}/E_{rev}) / (1 + \Sigma \eta_{pol}/E_{rev}) \quad (45)$$

The power of a cycle will be:

$$P = Q_{hs} \cdot \eta_{th} \cdot n_r / 60 \quad (46)$$

where: Q_{hs} - heat at the source of the engine; n_r – the speed of rotations per minute;

$\eta_{el} = Cw$ (proportional to the speed of the piston w). The trend of the curve $\eta_{th} = F(w)$ is always like in Fig. 7 and at the maximum of η_{th} correspond to zero speed; but the trend of $P = F(w)$ always has a maximum, which corresponds to the optimum value of the speed w_{opt} or $\eta_{r,opt}$.

The *Power* of a Fuel Cell or a Battery:

$$P_{FC,B} = \eta_{el} \cdot E_{rev} \cdot I \quad (47)$$

will also have a maximum for an *optimum current* I or *optimum density of the current* i . The *electrical efficiency* of a Fuel Cell or a Battery has a completely similar aspect like the efficiency of a thermal cycle (or thermal cycle engine). Using this method of optimization, we could express the Efficiency and Power of a cycle not only as a function of the speed but also as a function of some important dimensions of the engine. For example, for a Stirling solar engine we have done this with respect to the diameter of the tubes of Concentrated Solar Radiation Receiver and simultaneously optimized the speed of the engine and also its diameter d for different thermal agents (air, helium, hydrogen).

In conclusion the analogy pointed out in this section permits a unified treatment for optimization of thermal machines and electrochemical devices starting with the new expressions for the First Law for Processes with Finite Speed. This direct method could be the starting point of a new Non – Linear Irreversible Thermodynamics because two different fields have been studied with the same method.

7. CONCLUSION. THE IMPORTANCE AND SIGNIFICANCE OF THE DIRECT METHOD FROM FINITE SPEED THERMODYNAMICS (TFS) APPLIED FOR THERMAL MACHINES AND ALSO FOR ELECTROCHEMICAL DEVICES.

The method of analysis called by us the Direct Method proceeds from a basis of Thermodynamics Fundamentals, detailed and developed

systematically, starting from an unique equation (2) or (12) or (17), with The Equation of The First Law of Thermodynamics for Finite Speed Processes, combined with the Second Law. In order to shorten this expression, in all our papers and books, we have used the expression: THE FIRST LAW OF THERMODYNAMICS FOR FINITE SPEED PROCESSES.

The most important advantages of the method developed in the framework of TFS, in comparison with TFT, is that it is capable of being Validated and it explains and contains quantitatively both causes and mechanisms of irreversibility generation in complex cycles or real machines such as Stirling Machines (Engines, Refrigerators, Heat Pumps, Solar Stirling Motors), as well as in other cycles like: Otto, Diesel, Brayton and Carnot. **The explanation of this success consist in the fact that TFS takes into account both causes of irreversibilities: internal and external, all of them expressed as a function of the speed and other parameters, in the same unique Fundamental Equations: Eq. (12) - for Simple Systems or Eq. (17) - for complex Systems** [9], [10], [23], [24]. This unified approach is extremely important in the case of complex installations where Thermal Machines (TM) are combined with Electrochemical Devices (ED). Such Complex Systems are, for example, the SEHE-Systems (as we called them). **In a recent paper[54], we have used and developed recently this approach for Optimization of Solar Stirling Engines, producing electricity - used in a Electrolyzer, producing Hydrogen - stored by compression and used in the night in Fuel Cells, for producing backup electricity. A similar approach can be done in Optimization of Hybrid Cars where a Thermal Machine (internal combustion engine) is combined with an Electrochemical Device (a Fuel cell or a High Capacity Battery), increasing the total efficiency and also decreasing pollution.**

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