

IRREVERSIBLE FINITE SPEED THERMODYNAMICS (IFST) IN SIMPLE CLOSED SYSTEMS

I. Fundamental Concepts

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Rezumat. Lucrările de pionierat în dezvoltarea Termodinamicii cu viteză finită au fost scrise în perioada 1961-1972 de către L. Stoicescu și S. Petrescu [1-12]. Aceste lucrări inițiale au fost urmate de studii privind ireversibilitatea Proceselor Electrochimice, elaborate de către S. Petrescu, V. Petrescu, S. Sternberg et. al. [13-23]. Aceste cercetări au condus la generalizarea Principiului întâi al Termodinamicii pentru procesele cu viteză finită și pentru procesele electrochimice din sisteme ca: baterii, electroizoare și pile de combustie. Până la urmă toate aceste cercetări au condus la unificarea abordării mașinilor termice și a aparatelor electrochimice folosind o metodă unică, numită metoda directă [24-30, 33-35]. Această metodă se bazează pe faptul că Primul principiu pentru procesele cu viteză finită a fost aplicat într-un mod sistematic la sistemele complexe [23-29] ca motoare Stirling, refrigeratoare Stirling, pompe de căldură Stirling [26, 29, 34, 35, 37, 51, 52, 55, 56, 59, 65, 67, 68, 70] și la alte cicluri ca ciclul Carnot [30, 33, 55, 60-64, 66, 71], ciclul Otto [5, 57], ciclul Diesel [58, 69]. Aceste cercetări au condus în final la numeroase articole în reviste și conferințe precum și la 4 teze de doctorat [37, 51, 52, 55]. Urmărind această dezvoltare a domeniului Termodinamicii cu viteză finită ni se pare acum potrivit să sistematizăm și unificăm metoda directă prin folosirea a ceea ce am numit Metoda grafo-analitică de studiu și optimizare a mașinilor termice [24-30, 33-35]. Cu această lucrare începem publicarea într-o manieră sistematică, în revista *Termotehnica*, a unei serii de lucrări fundamentale care au condus treptat la dezvoltarea Termodinamicii ireversibile a proceselor cu viteză finită.

Cuvinte-cheie: termodinamică ireversibilă, procese cu viteza finita, cicluri ireversibile, metoda directă.

Abstract. The seminal papers in the development of the study of Finite Speed Processes were written in the time period between 1961 and 1972 by L. Stoicescu and S. Petrescu [1-12]. These initial papers were followed by studies of Irreversible Processes in Electrochemical Systems by S. Petrescu, V. Petrescu, S. Sternberg et. al. [13-23]. These studies resulted in the generalization of the First Law of Thermodynamics for Finite Speed Processes for Electrochemical Systems such as Batteries, Electrolysers and Fuel Cells. Ultimately, this led to a Unified approach to Thermal Machines and Electrochemical Devices using an unique method, called the Direct Method [24-30, 33-35]. 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. Meanwhile, a well-developed form of the First Law of Thermodynamics for Finite Speed Processes was applied in a systematic manner to Complex Systems [23-29] such as Stirling Engines, Stirling Refrigerators, Stirling Heat Pumps [26, 29, 34, 35, 37, 51, 52, 55, 56, 59, 65, 67, 68, 70] and to other cycles, for instance, the Carnot cycle [30, 33, 55, 60-64, 66, 71], Otto cycle [5, 57], Diesel cycle [58, 69]. These studies in turn led to numerous journal and conference papers and to 4 doctoral dissertations [37, 51, 52, 55]. With this background of accomplishment, it is now appropriate to systematize and unify the Direct Method by using what is termed the graphical / analytical method for Study and Optimization of Thermal Machines. [24-30, 33-35]. This Paper starts a Series of papers which conducted to the Development of Irreversible Thermodynamics with Finite Speed, which are going to be published in "Revista Termotehnica".

Keywords: irreversible Thermodynamics, Finite Speed Processes, Irreversible Cycles, Direct Method.

1. NEW CONCEPTS AND DESCRIPTIONS IN IRREVERSIBLE FINITE SPEED THERMODYNAMICS (IFST)

The piston and cylinder device shown in Fig. 1 illustrates the simplest closed system in which a finite speed irreversible process may take place. In this case, the only interactions between the system and the surroundings are a thermal one, δQ_{irr} , and a finite speed mechanical one, δW_{irr} .

In Irreversible Thermodynamics with Finite Speed, where conditions of non-equilibrium prevail, **new concepts and conditions are needed to describe the state of the system and the processes the system undergoes.** The analysis becomes much more complex than when considering classical reversible processes. However, **Finite Speed Thermodynamics** models real systems more closely both qualitatively and quantitatively.

Figure 2 illustrates some of these new concepts with regard to the pressure variation during the expansion process with Finite Speed.

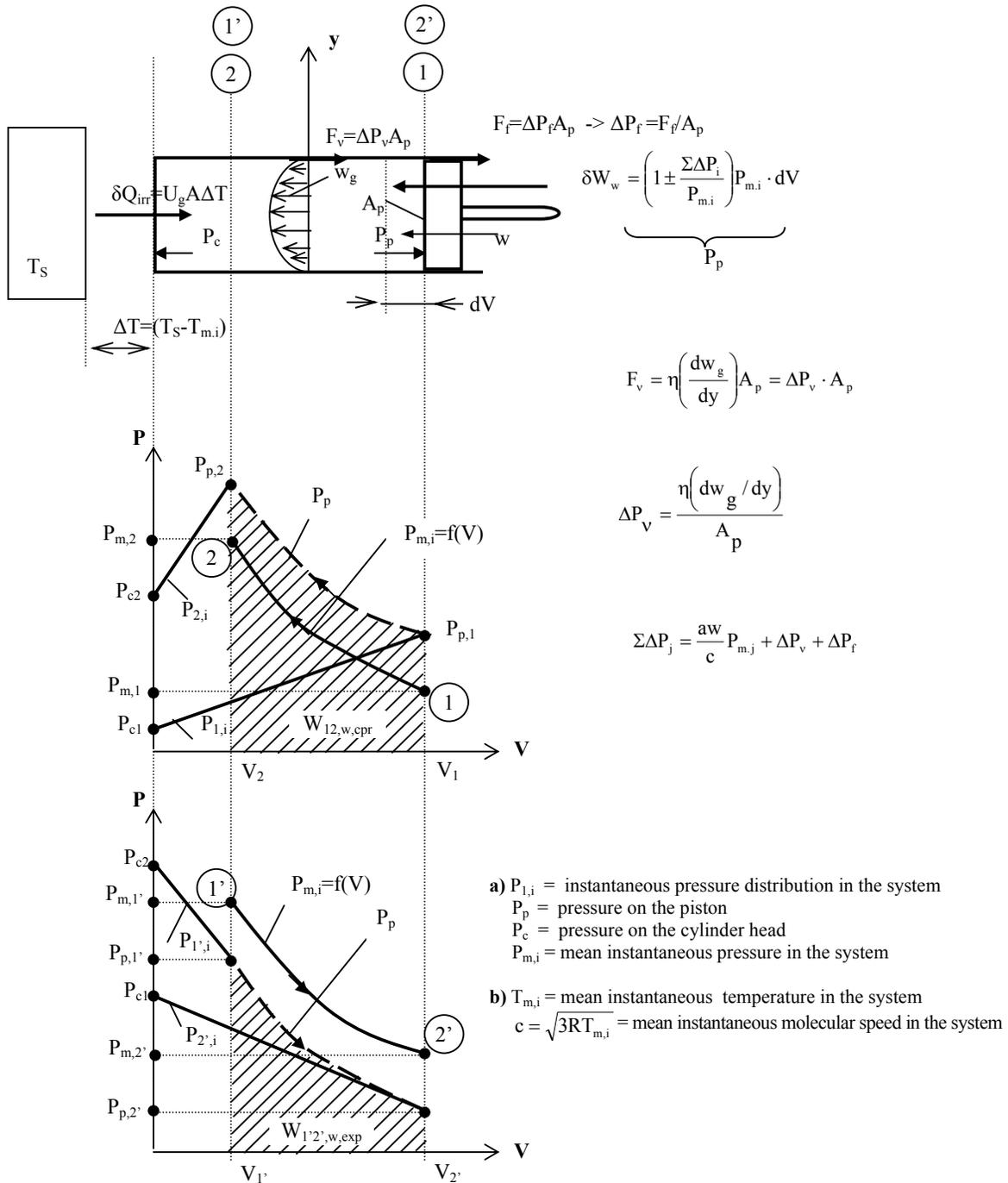


Fig. 1. Simple thermodynamic system in which an Irreversible Process with Finite Speed w evolves:
 a) Compression process; b) Expansion process.

a. Instantaneous pressure distribution in the system. The curve labeled P_{gas} describe in the new type of P-V diagram, necessary to be introduces in **The Irreversible Thermodynamics with Finite Speed**, the instantaneous pressure of the gas in the cylinder (system), for a certain moment in the time of the motion of the piston with the speed w . We do not know exactly how this distribution looks like, but in the simplest

approximation we could consider it as linear, as was represented in the figure 2.2, for simpler understanding of these new concepts.

b. Gas instantaneous mean pressure. The horizontal line indicates the uniform distribution that would occur in the system if the piston is stopped and the finite relaxation time of the system is achieved. This pressure $P_{gas,m}$ will be used as a basis for the description of the

processes in the system in place of the equilibrium pressure, p , from **Equilibrium-Reversible Thermodynamics**.

The main difference between what occurs in the Finite Speed processes compared to equilibrium-reversible processes, where the speed approaches zero, is that use of two pressures instead of only one is needed to properly describe finite speed processes. This is because in Finite Speed Thermodynamics the pressure of the system (gas) $P_{gas,m,i}$ and the pressure on the piston, P_p are different.

c. The pressure on the piston differs from the gas pressure at any point in the system, as shown by the pressure distribution curves of Fig. 2.1 and 2.2. During a compression process the pressure on the piston, P_p , will be greater than the pressure at any other point in the system. The pressure of the gas in the system reaches a minimum at the cylinder head, P_c . However, in the case of an expansion process, the pressure on the piston, P_p , will be less than the pressure in any other point in the system, reaching a maximum at the cylinder head, P_c , as shown in Fig. 2.1.b and 2.2.

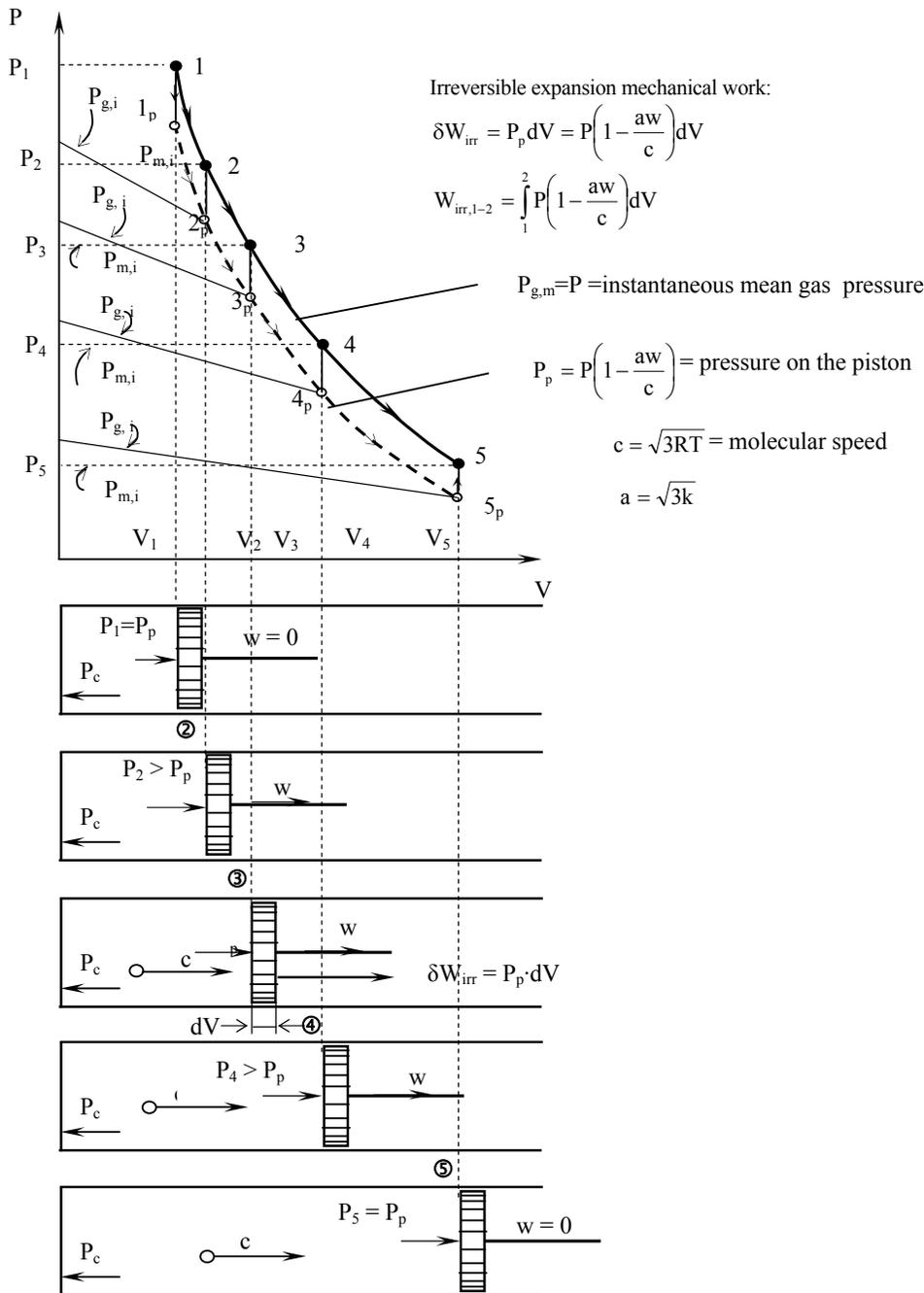


Fig. 2. Irreversible expansion process with finite speed.

Since it is impossible to use the *instantaneous pressure at every point* in the system at every instant during a process, the concept of an *instantaneous mean pressure*, $P_{gas,m,i}$ [1, 2, 8] is needed. This pressure differs from the *instantaneous pressure on the piston* at any instant. During compression $P_p > P_{gas,m,i}$ and during expansion

$$P_p < P_{gas,m,i},$$

as shown in Fig. 1a and 2.

d. The two parameters that will be used as the basis for analysis of the system are:

- the *instantaneous mean pressure in the gas* (in the system), $P_{m,i} = P_{gas,m,i}$ and
- the *instantaneous pressure on the piston* P_p .

This implies that a *Finite Speed Process* cannot be described on p-V coordinates by a single curve as can be done for classical *Reversible Processes*, but requires two curves [2, 3] - as shown on Fig. 1 and 2.

A better perspective on the important differences between classical *Reversible Equilibrium Thermodynamics* (RET) and the new *Finite Speed Irreversible Thermodynamics* (FSIT) may be gained by referring to Fig 3. The pressure during simple reversible compression and expansion processes is shown in Fig. 3a and 3c for purposes of comparison with the more complex plot of pressure during irreversible compression and expansion as shown on Fig. 3b and 3d. It might also be noted that the irreversible processes were plotted using the simplification of only the two parameters, P_p and P_m ,

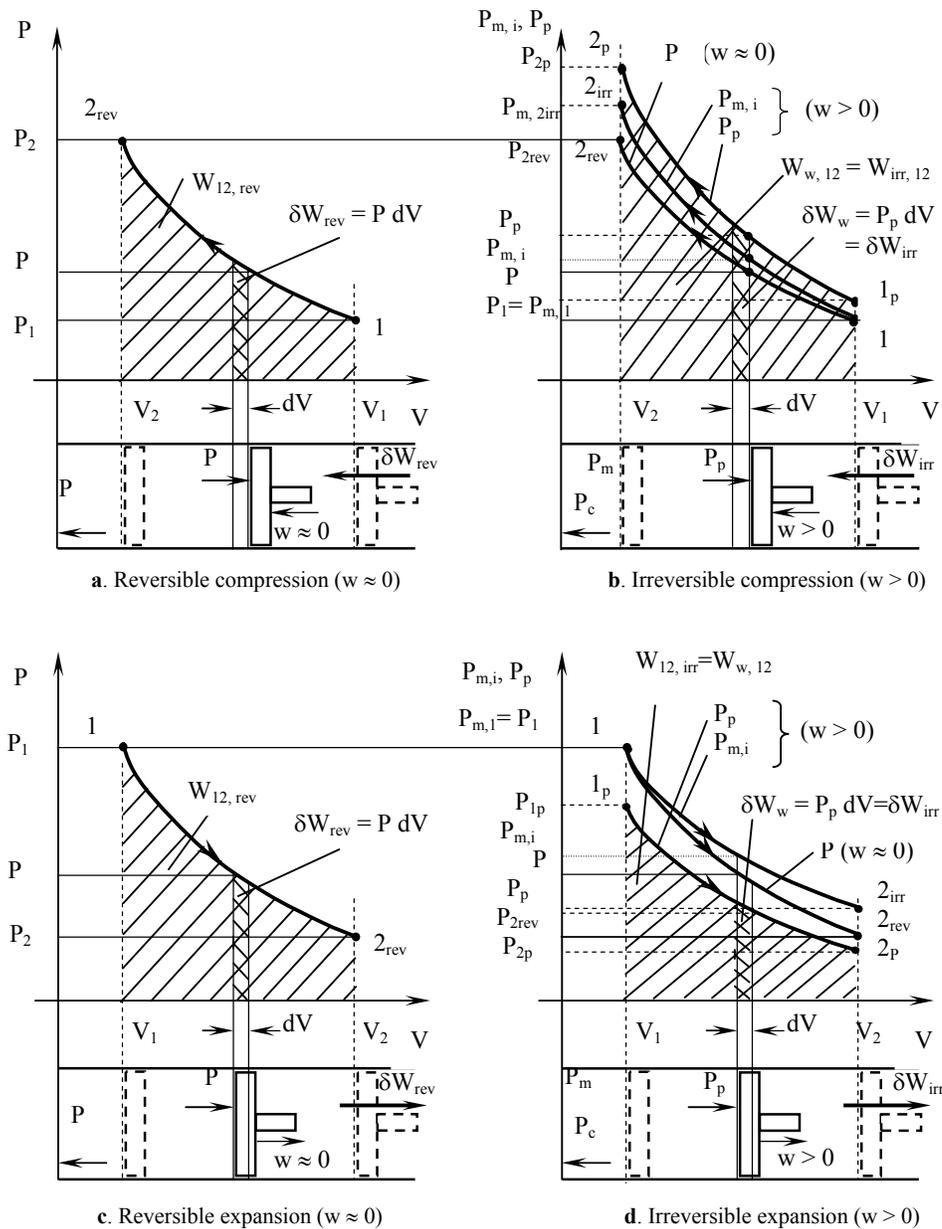


Fig. 3. Comparison between P-V diagrams for reversible and irreversible processes.

d. Comparison between reversible processes and irreversible processes with finite speed during compression and expansion (See Figure 3). The reversible compression process $1-2_{rev}$ in Fig. 3a overlaps, the reversible expansion process $1-2_{rev}$ in Fig. 3c. Therefore the areas under these two curves, which represent the work of compression and the work of expansion respectively, are equal and the net work is zero. When the irreversibility due to finite speed is considered, two curves are needed to describe each process, as shown by the curves 1_p-2_p and $1-2_{irr}$ in Figs. 3b and 3d. These curves during the compression process differ from those during the expansion process.

Consequently, the system reaches a different state than the initial one after the compression process and also after the expansion process. Thus, point 2_{irr} in Fig. 3d differs from point 1 in Fig. 3b and, in particular, the area under the pressure curve during compression differs from the area under the pressure curve during expansion. Accordingly, the net mechanical work is different. It is reduced in proportion to the difference between these areas. The difference between the work of adiabatic compression and expansion is clearly shown in Fig. 4 as the difference between the area under the curve $1_{p,c}-2_{p,c}$ during the compression process and the area under the curve $2_{p,e}-3_{p,e}$ during the expansion process.

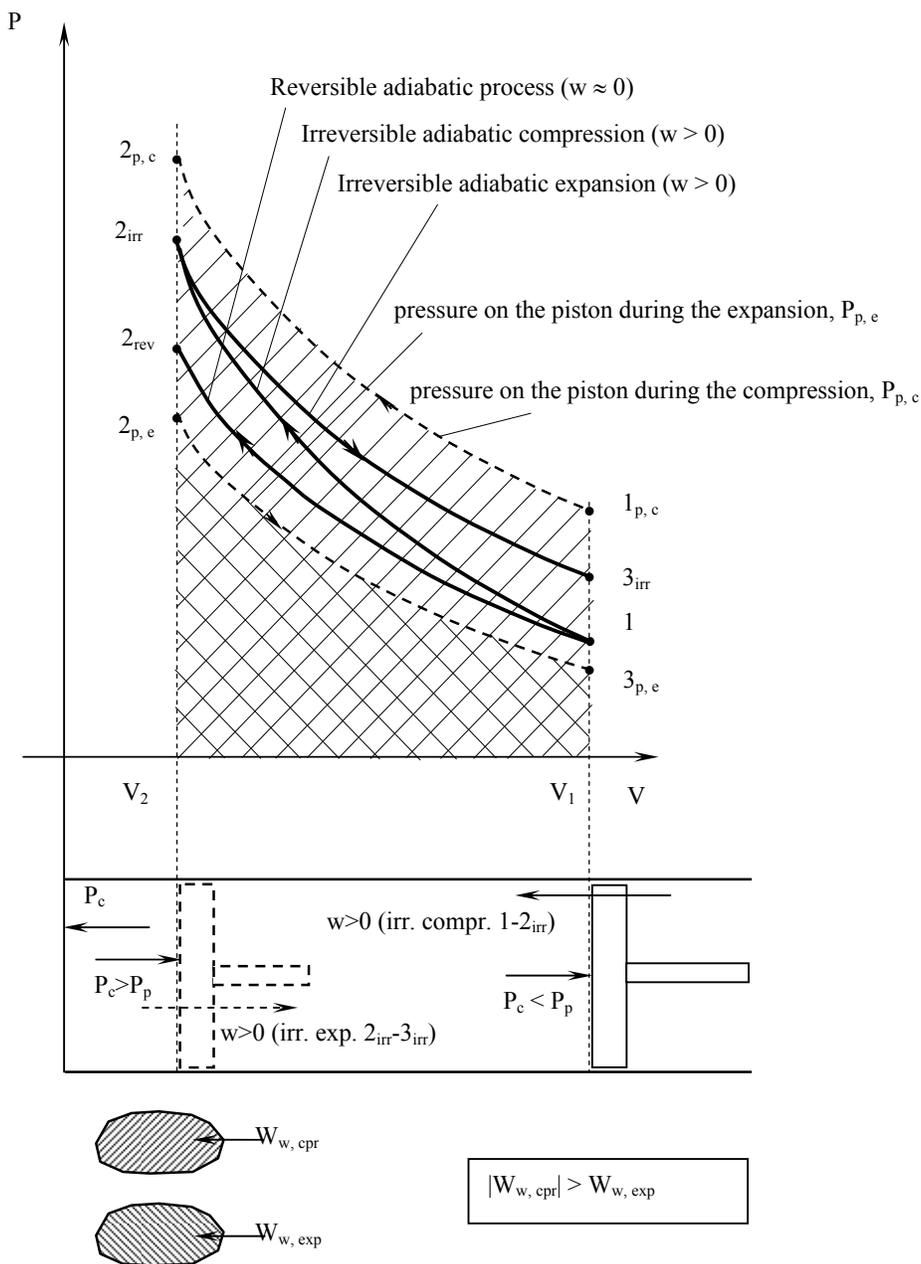


Fig. 4. Adiabatic compression with finite speed, $1-2_{irr}$, followed by adiabatic expansion with finite speed, $2_{irr}-3_{irr}$, compared with reversible adiabatic compression and expansion ($w \approx 0$), $1-2_{rev}$.

2. RESULTS OF APPLYING THE FIRST LAW OF THERMODYNAMICS FOR PROCESSES WITH FINITE SPEED

Use of the **First Law of Thermodynamics for Finite Speed Processes** to optimize the theoretical cycles of actual thermal machines is the principal focus of this analysis. The Direct Method of application of the First Law to processes with finite speed is used. It forms the basis of the graphical/ analytical technique that will be employed in the analysis.

A logical sequence for presenting this analysis for optimization of thermal machines, which also largely corresponds to the historical development, is as follows:

- The First Law for Finite Speed processes in closed simple systems.
- Finite Speed Processes in closed simple systems.
- Finite speed Cycles in closed simple systems.
- Graphical and analytical methods for finite speed cycles in closed simple systems.

This forms a background for proceeding to consideration of closed complex systems such as Stirling Machines. In Stirling Machines heat is transferred to and from the working gas internally through regenerative processes and heat is also transferred to the working gas from the hot source and from the working gas to the cold sink. These processes are accomplished through the motion of two pistons in cylinders.

A variety of Stirling Machines, operating as engines or reversed as refrigerators or heat pumps, are in commercial service. The performance of these machines is known as is their dimensions and operating conditions. The Stirling Machine therefore is a very good model to use as a basis for validation of **Irreversible Finite Speed Thermodynamic Theory** using the **Direct Method**. These graphic/analytic techniques yield results that can be compared to operating parameters obtained from these existing machines, so the degree of validity of the theory in predicting performance can be determined. For complex systems with internal heat exchangers, the method validation step forms an important part of the presentation of the analysis in addition to the four elements cited above. It is possible to validate FSIT by using the Direct Method and applying the graphic/analytic technique. This is why this new analysis technique for irreversible thermodynamic processes has power that is equivalent to that of a **new research instrument for Designing and Optimizing Thermal Machines**. It should be noted however that this validation step is generally not possible when using the widely discredited analytical method known as **Finite Time Thermodynamics** [31, 32, and 36].

The method of analysis we present proceeds from a basis of thermodynamic fundamentals, detailed and developed systematically, starting from an unique equation, that is **The Equation of The First Law of Thermodynamics for Finite Speed Processes**. The advantages of this method are that it is capable of being validated and it explains both the causes and mechanisms of irreversibility

generation in complex cycles or real machines such as Stirling Machines [23, 26, 29, 34, 35, 37, 51, 52, 55, 56, 59, 61, 65, 6, 68, 70] Otto Cycle [5, 57], Diesel Cycle [58, 60], Carnot Cycle [23, 30, 33, 39, 55, 60-64, 66, 71].

3. THE FIRST LAW OF THERMODYNAMICS FOR FINITE SPEED PROCESSES IN CLOSED SIMPLE SYSTEMS

3.1. First Law for Reversible and Irreversible Processes

For a closed simple system in which the piston-cylinder friction and internal gas viscosity effects are neglected, as shown in Fig. 3b and 3d, the mathematical expression of the **First Law for Finite Speed Irreversible Processes** will be:

$$dU_{\text{irr}} = \delta Q_{\text{irr}} - \delta W_{\text{irr}} \quad (1)$$

This expression is identical to the expression for reversible processes. When the piston speed approaches zero, the process may be accurately modeled as approaching reversibility and the expression for reversible processes is given by:

$$dU_{\text{rev}} = \delta Q_{\text{rev}} - \delta W_{\text{rev}} \quad (2)$$

Nevertheless, it is important to note that the meaning in RET is different than in FSIT.

3.2. Internal Energy Change in Irreversible Finite Speed Processes

As it is well-known, dU_{rev} , which is denoted only by dU in RET, represents the **reversible internal energy variation** of the system as it passes through successive equilibrium states, while dU_{irr} represents the **irreversible internal energy variation** of the system as it passes through successive non-equilibrium states. In RET the specific internal energy, u , is uniform throughout the system so:

$$U = U_{\text{rev}} = mu \quad (3)$$

A similar expression is not possible for processes in IFST, since in IFST the pressure and temperature vary from one point to another at each instant and also vary with time at each point during the processes. Therefore, it is necessary to introduce the concept of an **instantaneous mean temperature**, $T_{m,i}$ and an **instantaneous specific internal energy**, $u_{m,i}$ similarly to the introduction of the concept of **instantaneous mean pressure**, $P_{m,i}$. Using these concepts, the following relationships follow:

$$U_{\text{irr}} = \int_{\text{system}} u \cdot dm = m \cdot u_{m,i} \quad (4)$$

Joule's equation for an ideal gas is:

$$dU_{\text{irr}} = m \cdot du_{m,i} = mc_v \cdot dT_{m,i} \quad (5)$$

The corresponding expression when RET is considered is:

$$dU_{\text{rev}} = mc_v \cdot dT \quad (6)$$

Eqs. 5 and 6 appear to be almost the same but they are not. It is important to note the meaning of $T_{m,i}$ and the means for determining it, both theoretically and through actual measurement. These computations are more complex in FSIT than in RET.

However, the total change in the internal energy for a process such as 1-2, as shown in Fig. 3, can be determined by integration of eqs. 2-5 to obtain:

$$\Delta U_{\text{irr}} = (U_2 - U_1)_{\text{irr}} = mc_v (T_{m,2} - T_{m,1}) \quad (7)$$

The corresponding expression for RET is:

$$\Delta U = mc_v (T_2 - T_1) \quad (8)$$

and although this expression appears similar to eq. 2-7, it must be noted that $T_{m,2}$ is not only conceptually different from T_2 , but it is usually also quantitatively different. $T_{m,2}$ is the *instantaneous mean temperature at state 2*, while T_2 is the *equilibrium temperature at state 2*, which is uniformly distributed throughout the system.

For most **Finite Speed Irreversible Processes**:

$$(T_2 - T_1) = \Delta T_{\text{rev}} \neq \Delta T_{\text{irr}} = (T_{m,2} - T_{m,1}) \quad (9)$$

This is true if the process begins at the same initial state 1 and if change in volume ΔV is the same since:

$$T_2 \neq T_{m,2} \quad (10)$$

The only exception occurs in the case of isothermal processes where:

$$T_1 = T_2 = T_{m,2} \quad (11)$$

Analysis of the isothermal process appears at first glance to be very simple, but it is actually among the more complex of finite speed processes. The isothermal process occurs in Carnot, Stirling, Ericsson and other theoretical cycles, so it merits particularly careful attention. A clear understanding the isothermal process is fundamental to understanding these cycles [54].

3.3. Irreversible Work in Finite Speed Processes

Another matter of importance is the determination of mechanical work. In Reversible Thermodynamics, the expression for the *reversible mechanical work* is:

$$\delta W_{\text{rev}} = P \cdot dV \quad (12)$$

In FSIT the expression for the *irreversible mechanical work* is:

$$\delta W_{\text{irr}} = P_p \cdot dV \quad (13)$$

As shown in Fig. 4, the *pressure exerted on the piston* is not the same as the *instantaneous mean pressure of the gas* in the cylinder, $P_{m,i}$. Consequently, **one of the most important problems in the development of FSIT is to find an expression for P_p as a**

function of $P_{m,i}$ and various other parameters of the system, such as, piston speed, w , instantaneous mean temperature, $T_{m,i}$.

The **Direct Method** and, following it, the graphical/analytical technique were developed to solve this problem. The solution is fundamental and central to FSIT. Accordingly, it is presented in detail in the following analysis.

To determine the pressure on the piston an expression involving the physical parameters of the system are needed. Such an expression takes the form:

$$P_p = f(P_{m,i}, w, T_m, R, k, \dots) \quad (14)$$

The need for an explicit form of eq. 14 is illustrated by the following reasoning.

An expression of the First Law for finite speed processes in closed simple systems can be written by substituting eq. 5 and 12 into eq. 1. The result is:

$$mc_v dT_{m,i} = \delta Q_{\text{irr}} - P_p \cdot dV \quad (15)$$

If the state equation for an ideal gas is written in terms of *instantaneous mean parameters*,

$$P_{m,i} \cdot V = mRT_{m,i} \quad (16)$$

is substituted into eq. 15, it would appear that any **Finite Speed Irreversible Process** in the system could be analyzed, whether isobaric, isometric, isothermal, adiabatic, or polytropic. The difficulty, however, is that eq. 15 does not contain $P_{m,i}$, but instead P_p and this P_p is not equal to $P_{m,i}$. This simply points out **the need to find an expression for the pressure P_p as a function of $P_{m,i}$, w , and other relevant parameters**. Developing such an expression was the thrust of a doctoral dissertation [2] and numerous articles in the scientific literature [1, 6, 7, 8, 9, 10, and 11].

One aspect of finding an expression for the pressure on the piston in closed simple systems is to consider the kinetic-molecular and phenomenological models used by Macke [49] and Sommerfeld [50]. These models [1, 2, 7, 8, and 9] consider the *piston speed* and the *average molecular speed* (or the *speed of sound*) in the working gas as follows.

1°. **The basic kinetic-molecular model** [1, 2] led to the following relationship:

$$\delta W_{\text{irr}} = P_{m,i} \cdot \left[1 \pm \frac{aw}{c} + \frac{bw^2}{c^2} \pm \dots \right] \cdot dV = P_p \cdot dV \quad (17)$$

where $a = 2$; $b = 5$; and $c = \sqrt{3RT_{m,i}}$ = *average speed of molecules* computed at the *instantaneous mean temperature*, $T_{m,i}$.

2°. **The advanced kinetic - molecular model** [8, 9], is based on a Maxwell-Boltzmann distribution and of a finite relaxation time in the system. It led to:

$$\delta W_{\text{irr}} = P_{m,i} \cdot \left[1 \pm 2,764 \frac{w}{c} + 3 \frac{w^2}{c^2} \pm 1,283 \frac{w^3}{c^3} + \dots \right] \cdot dV \quad (18)$$

3°. **The phenomenological model of the interaction between piston and gas** is based on the hypothesis of pressure wave propagation generated by the *Finite Speed of the Piston* and the *speed of sound* in the gas [1, 2]. It led to:

$$\delta W_{\text{irr}} = P_{m,i} \cdot \left[1 \pm \frac{aw}{c} \right] \cdot dV \quad (19)$$

where $a = \sqrt{3k}$, k is the specific heat ratio and $c = \sqrt{3RT_{m,i}}$.

Eq. 19 can be also written as a function of the *speed of sound*, c_s , instead of the *average speed of molecules*, c . The *speed of sound* is:

$$c_s = \sqrt{kRT_{m,i}} \quad (20)$$

Eq. 2.19 may also be written in terms of the *speed of sound* by letting $a = \sqrt{3k}$ in the expression for the *average speed of molecules* and substituting eq. 20 into eq. 19 as follows:

$$\begin{aligned} \delta W_{\text{irr}} &= P_{m,i} \cdot \left[1 \pm \frac{\sqrt{3k} \cdot w}{\sqrt{3RT_{m,i}}} \right] \cdot dV = \\ &= P_{m,i} \cdot \left[1 \pm \frac{k \cdot w}{\sqrt{k} RT_{m,i}} \right] \cdot dV = \\ &= P_{m,i} \cdot \left[1 \pm k \left(\frac{w}{c_s} \right) \right] \cdot dV \end{aligned} \quad (21)$$

The *ratio of the piston speed to the speed of sound in the gas* is w/c_s . This ratio is also the *Mach number*, M , so:

$$\delta W_{\text{irr}} = P_{m,i} [1 \pm k \cdot M] \cdot dV \quad (22)$$

Use of eq. 22 for calculating work is preferable in most applications since it is both simple and non-dimensional.

4°. **The Linear Irreversible Phenomenological Thermodynamics (LIPT) model** [7], applied to finite speed interactions between the gas and piston, led to the expression:

$$\delta W_{\text{irr}} = P_{m,i} [1 \pm K_I \cdot w] \cdot dV \quad (23)$$

where K_I is a constant which depends on the properties and *instantaneous mean temperature* of the gas. The theory can neither explain, nor estimate the value of this constant, when it occurs in other phenomena. However, by comparing eq. 23 with eq. 17, K_I is evaluated as:

$$K_I = \frac{2}{\sqrt{3RT_{m,i}}} \quad (24)$$

Similarly, comparison of eq. 23 to eq. 18 results in:

$$K_I = \frac{2,764}{\sqrt{3RT_{m,i}}} \quad (25)$$

and comparison of eq. 23 to eq. 19 results in:

$$K_I = \frac{\sqrt{3k}}{\sqrt{3RT_{m,i}}} = \frac{k}{\sqrt{kRT_{m,i}}} = \frac{k}{c_s} \quad (26)$$

3.4. Heat Transfer with Finite Speed

Having the above expressions for evaluating the work term, attention now can be devoted to the heat transfer term in the first law for finite speed simple systems as given in eq. 1. The irreversible heat transfer, δQ_{irr} is generated by the existence of a temperature gradient between the gas and an exterior heat source. Since a temperature distribution exists within the system, the instantaneous mean temperature, $T_{m,i}$, is used to characterize the system. When heat passes through a solid wall from an exterior fluid to the fluid inside a system, the term δQ_{irr} can be expressed as:

$$\delta Q_{\text{irr}} = \dot{Q} \cdot dt = U_g \cdot A \cdot (T_{m,i} - T_s) \cdot dt \quad (27)$$

where: U_g represents the global heat transfer coefficient.

When the heat source is the cylinder wall, U_g becomes equal to h_{cv} , the convection coefficient, which in turn depends on the speed of the fluid inside the cylinder, its temperature and the system fluid properties.

The cross-sectional area for heat transfer, A , between the heat source and the gas in the cylinder may be either a constant or variable function of the piston position. A mean area can be used whenever the actual area varies.

Substitutions can now be made into eq. 1 to obtain an initial expression for the First Law for finite speed processes in simple systems. Substitution for δQ_{irr} , as evaluated in eq. 27 and δW_{irr} , as evaluated in eq. 17, results in the expression:

$$\begin{aligned} dU_{\text{irr}} &= U_g A (T_{m,i} - T_s) \cdot dt - \\ &- \left[1 \pm \frac{aw}{\sqrt{3RT_{m,i}}} + \frac{bw^2}{3 RT_{m,i}} \pm \dots \right] \cdot P_{m,i} \cdot dV \end{aligned} \quad (28)$$

The equation for the First Law for finite speed processes in simple systems is valid regardless of the working fluid when written in this form. When the working fluid is an ideal gas, the expression for dU_{irr} , from eq. 2.5, the Joule equation, may be substituted in eq. 28. Upon substitution and using instantaneous mean temperatures, eq. 28 becomes:

$$\begin{aligned} mc_v dT_{m,i} &= U_g A (T_{m,i} - T_s) \cdot dt - \\ &- \left[1 \pm \frac{aw}{\sqrt{3RT_{m,i}}} + \frac{bw^2}{3 RT_{m,i}} \pm \dots \right] \cdot P_{m,i} \cdot dV \end{aligned} \quad (29)$$

This equation is applicable to finite speed irreversible processes in simple systems in which the working substance is an ideal gas. However, eq. 29 cannot be

integrated for, for instance, isothermal, adiabatic, polytropic or other specific processes, since it contains more than two variables. The number of variables will be reduced to two by first noting that the time increment $d\tau$, considered positive, equals the absolute volume of the working gas in the cylinder divided by the speed of the piston times the area of the piston, or:

$$d\tau = \frac{|dV|}{wA_p} \quad (30)$$

In the above relationship, the absolute value of the volume $|dV|$ is used because dV implies a (-) sign for compression and a (+) sign for expansion. Substituting eq. (30) into eq. (29) gives:

$$mc_v dT_{m,i} = U_g A (T_{m,i} - T_S) \cdot \frac{|dV|}{wA_p} - \left[1 \pm \frac{aw}{\sqrt{3}RT_{m,i}} + \frac{bw^2}{3RT_{m,i}} \pm \dots \right] \cdot P_{m,i} \cdot dV \quad (31)$$

In order to satisfy the sign convention for heat, the first term on the right-hand side of eq. 31 must be positive when heat is received by the system and must be negative when heat leaves the system. Therefore, a \pm sign is applied as a coefficient to U_g .

This allows rewriting $|dV|$ as dV in eq. 31 and this overcomes what would otherwise present a problem in integrating the expression.

The *instantaneous mean pressure*, $P_{m,i}$, as expressed by the state equation for an ideal gas, is:

$$P_{m,i} = \frac{mRT_{m,i}}{V} \quad (32)$$

Upon substitution into eq. 31 for the sign convention and pressure, $P_{m,i}$, one gets:

$$mc_v dT_{m,i} = \pm U_g A (T_{m,i} - T_S) \cdot \frac{dV}{wA_p} - \left[1 \pm \frac{aw}{\sqrt{3}RT_{m,i}} + \frac{bw^2}{3RT_{m,i}} \pm \dots \right] \cdot \frac{mRT_{m,i}}{V} \cdot dV \quad (33)$$

where (+) is for compression and (-) is for expansion processes.

The sign convention can be shown to be correct in eq. 33 by noting that during a compression process $dV < 0$ and the coefficient of the term has a + sign. This results in the term being negative. When $T_{m,i} > T_S$, the term $(T_{m,i} - T_S)$ is positive so the heat transfer term will be negative. This corresponds to heat leaving the system and is consistent with the customary sign convention for heat transfer. Conversely, when $T_{m,i} < T_S$, the heat transfer term is positive and this is consistent with the sign convention for a system receiving heat.

Eq. 33 can be further simplified by writing it in a non-dimensional form. This is accomplished by dividing each term of the equation by $mRT_{m,i}$. This results in a non-dimensional expression in two variables, a

non-dimensional temperature and a *non-dimensional volume* [25]:

$$\frac{c_v \cdot dT_{m,i}}{RT_{m,i}} = \left[\pm \frac{\alpha_g AV}{w A_p m R} \left(1 - \frac{T_S}{T_{m,i}} \right) - \left(1 \pm \frac{aw}{\sqrt{3}RT_{m,i}} + \frac{bw^2}{3RT_{m,i}} \pm \dots \right) \right] \cdot \frac{dV}{V} \quad (34)$$

We can call the eq. (34) the **Fundamental Equation of Irreversible Thermodynamics with Finite Speed** [25].

Unfortunately, the variables in this expression cannot be separated so straight forward integration is not possible. However, the expression can be solved by:

1) Numeric integration, which is very accurate, but does not offer an analytic equation for describing finite speed processes;

2) Integration for particular cases, which will be exemplified in the next papers;

3) Estimating some mean parameters during the process and after that, improving the numerical solution by successive iterations.

In the next Papers we are going to show how this Expression of the **First Law for Irreversible Processes** (eq. 34) can be used in order to obtain the equations of **Finite Speed Processes**, and after that how we can use these equations for the **Study and Optimization of any Thermodynamical Cycles**, using **The Direct Method**.

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