
I. Matter behaviour. Energy, work, heat and efficiency, generally and in gases

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General considerations about the work and heat, about the laws of matter behavior was followed by energy analysis as a unitary concept for description of processes in gases, liquids and solids. One puts into evidence the action and effect energy, the energy for volume variation and the energy for shape variation. The deformation processes in gas volume, treated from thermodynamic point of view, is the origin of work and heat calculation in perfect gases processes, as well as in ideal gases in the case of irreversible processes. These were followed by discussion concerning the internal energy variation polytropic and adiabatic processes. The First Law of Thermodynamics for reversible processes, as well, for irreversible processes with finite speed have been presented and discussed. The influence of the process speed, as well as the efficiency and degree of irreversibility, have been presented from the Thermodynamic and Energetic point of view. The numerical examples show how the results obtained in the paper may be practical used.

Key words: matter behavior; energy, work and heat; thermodynamic irreversible processes; gases; efficiency.

Throughout a thermo-mechanical process, the state parameters of the matter involved in the process get modified. The choice of parameters and the extent to which they are modified depend on the aggregation state of the matter involved. However, even within the same aggregation state, the result of the thermomechanical process depends on matter behavior. For this reason, in any analysis of a thermomechanical process one should start from the behavior law of the matter involved.

If we refer to present day thermodynamics one finds that generally, it starts with the enunciation of the principles of thermodynamics, then a single general law of behavior is stated and used (corresponding to an idealized model) namely the law of perfect gases [1]. By paraphrasing the title of C. Truesdell book „The Tragicomedy of Classical Thermodynamics” [2] we might say that the „drama of Thermodynamics” springs from the fact that thermodynamics foremost refers to the gaseous or vapour state, for which one uses the state law of perfect gases, the only law of behavior in thermodynamics (the 200 state equations for real gases and vapours being actually just approximates).

By using the law of perfect gases (which describes only a static state of the thermodynamic system) one defines these idealized thermodynamic processes where a constant state parameter is maintained (isobaric, p = constant, isothermal, T = constant, isochoric, V = constant). Then one defines and calculates two process quantities: thermodynamic work, W (measure of mechanical interaction), and thermodynamic heat, Q (measure of thermal interaction). The other two idealized thermodynamic processes, adiabatic and polytropic, are defined in a different way from the three processes above mentioned. Thus, the adiabatic one, is defined through the absence of an interaction, namely zero heat exchange with the environment (Q = 0), while the polytropic one is defined based on an equation named the equation of the polytropic process: \( pV^n = \text{constant} \) (\( n \) – polytropic exponent).

The internal energy is a concept whose value is calculated with a mathematical relation wherein matter behavior acting on it should be present (mechanical, thermal, electrical, magnetic, radiating etc.). From the viewpoint of behavior, matter cannot be placed in the same category as gas, liquid or solid only based on its state of aggregation, but based foremost on the loading conditions. A material in the liquid state loaded under great speed may behave like a solid. Likewise, a material in the solid state loaded over a very long span (hence at very very low speed), in certain conditions, can behave – partially at least – as a liquid (example: „the downstream flow of icebergs” or the „flow of the windows glasses”). The solid and liquid states further considered refer to the behavior of a solid body and the behavior of a liquid body.

Heat and work are not state properties but process (or interactions) quantities which is why they represent (qualitatively and quantitatively) energy exchanged by the system with the environment during the process.

Heat resulting in a process (thermodynamic, chemical, mechanical, electrodynamic a.s.o) is identified by means of perception and calculated by means of the behavior laws of the matter involved in the process. For the same value of the applied pressure, gases feature relatively high volume variation (\( \Delta V \neq 0 \)), unlike liquids and solids whose volume variation is very low. That is the reason one considers that the deformation of solids occurs at constant volume (\( \Delta V = 0 \)) while liquid flow occurs under constant density, which is the same as \( \Delta V = 0 \).

The calculation of work W and heat Q from Classical Reversible Thermodynamics, based on the laws of perfect gases (which correlates temperature with pressure and volume) does not apply to solids and liquids (in mechanics and electrodynamics), since for these matter states, generally, \( \Delta V \rightarrow 0 \). However, if we correlate the heat
resulting from the processes of flow, deformation or transmission of electrical energy through conductors, with the matter behavior laws specific to these processes, one obtains adequate expressions for work and heat in the processes involving liquids and solids.

In this way, both heat as well as work become quantities that can be calculated on the basis of the behavior laws of the matter that has been processed. Such an approach to the problem is possible on the basis of Energonics [3], where energy is correlated with the matter behavior (linear or nonlinear).

We shall further deduce the equations of the two process quantities intervening in the mathematical expression of the First Law of Thermodynamics (work and heat), in a unitary manner, based on the concepts of Energonics [3].

**Some laws of matter behavior**

The concepts used in equations describing behavior laws depend on the state of the matter under load.

Although nature is a unitary whole, for convenience, man has divided the physical universe into domains depending on the nature of action and/or effect obtained (Mechanics, Chemistry, Thermodynamics, Electricity, Magnetism, Biology, Geology etc.). Each of these disciplines is based, among others, on concepts, laws and individual correlations.

In Table 1 there are presented the laws of behavior corresponding to the simple loading [4]. They underlie some of the chapters science has been broken down into. In solving the problems of mechanical loading one still resorts to the laws of linear behavior (Hooke's law, (1) and (2)) and rarely to those of nonlinear behavior (3) and (4)). In solving the problems of current fluid (also called Newtonian) flow one resorts to the laws of linear behavior (Newton's law (5)). One resorts to the laws of nonlinear behavior (6) for some other fluids like solutions, polymer melts etc. (called non-Newtonian fluids).

Some fluids possess both fluid characteristics (viscosity), as well as solid body characteristics (elasticity); they behave viscoelastically (relations (5) – (8)). The behavior of some viscoelastic fluids [4] under simple shear stress may be described as in Voight – Kelvin’s law

$$\tau = G \cdot \gamma + \mu \cdot \dot{\gamma}.$$  

### Table 1

**BEHAVIOR LAWS, NOWADAYS USED IN SOME CHAPTERS OF SCIENCE**

<table>
<thead>
<tr>
<th>Chapters of Science</th>
<th>Behavior law under simple loading</th>
<th>Type of deformation and other particularities</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.</strong> Theory of Elasticity; Strength of Materials etc.</td>
<td>- linear: $\sigma = E \cdot \varepsilon$ - Hooke’s law (1)</td>
<td>- Corresponds to loading under the creep temperature of solid bodies;</td>
</tr>
<tr>
<td></td>
<td>$\tau = G \cdot \gamma$ (2)</td>
<td>- uniaxial elongation loading at constant volume, free of flow;</td>
</tr>
<tr>
<td></td>
<td>- nonlinear: $\sigma = M \cdot \varepsilon$ (3)</td>
<td>- thermal effects are neglected.</td>
</tr>
<tr>
<td></td>
<td>$\tau = M \cdot \dot{\gamma}$ (4)</td>
<td></td>
</tr>
<tr>
<td><strong>2.</strong> Fluid Mechanics; Aerodynamics; Rheology etc.</td>
<td>- linear: $\tau = \mu \cdot \dot{\gamma}$ - Newton’s law (5)</td>
<td>- Refers to fluid simple shear flow;</td>
</tr>
<tr>
<td></td>
<td>- nonlinear: $\tau = K \cdot \dot{\gamma}$ - Ostwald – de Waele’s law (6)</td>
<td>- volume deformation is neglected;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- used for calculating the energy dissipated through internal friction.</td>
</tr>
<tr>
<td><strong>3.</strong> Rheology; Viscoelasticity etc.</td>
<td>- linear: $\tau = \mu \cdot \dot{\gamma}$ - Newton’s law (5)</td>
<td>- Simple shear and volume deformation flow (normal stress effect);</td>
</tr>
<tr>
<td></td>
<td>$\sigma = \mu \cdot \varepsilon$ - Troutton’s law (7)</td>
<td>- used for determining the flow thermal effects (caused by shear stress $\tau$) and elastic effects (caused by normal stresses $\sigma$).</td>
</tr>
<tr>
<td></td>
<td>- nonlinear: $\tau = K \cdot \dot{\gamma}$ - Ostwald – de Waele’s law (6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma = K \cdot \varepsilon$ (8)</td>
<td></td>
</tr>
<tr>
<td><strong>4.</strong> Electrochemistry; Electricity etc.</td>
<td>- linear: $U = R \cdot I$ - Ohm’s law (9)</td>
<td>- Refers to electron „flow” through electric conductors;</td>
</tr>
<tr>
<td></td>
<td>- nonlinear: $U = M \cdot I^2$ (10)</td>
<td>- used to calculate the thermal effect of the electric current;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- magnetic effect is neglected.</td>
</tr>
<tr>
<td><strong>5.</strong> Thermodynamics</td>
<td>- nonlinear: $p \cdot \nu = constant$ (11)</td>
<td>- Refers to gas volume deformation;</td>
</tr>
<tr>
<td></td>
<td>or $p \cdot \dot{V} = m \cdot \dot{T}$ (12)</td>
<td>- does not refer to gas flow.</td>
</tr>
</tbody>
</table>

$\sigma$ – normal stress; $\tau$ – shear stress; $E$ – longitudinal modulus of elasticity or Young modulus; $G$ – shear modulus or transverse elasticity modulus; $\varepsilon$ – strain; $\dot{\gamma}$ – shear strain; $\dot{\varepsilon}$ = $dy/dt$ – shear rate; $k$ = $dk/dt$ – extensional strain rate; $t$ – time; $M$; $M'$; $K$; $K'$; $M_p$ – factors, constants of material under load; $k_i$; $v_i$; $n_i$ – exponents, constants of material under load; $\mu$ – shear viscosity; $\mu_e$ – extensional or elongational viscosity; $U$ – Voltage; $I$ – electric current intensity; $R_e$ – electrical resistance; $p$ – pressure; $V$ – volume; $T$ – temperature; $m$ – perfect gas mass; $R$ – universal constant of perfect gases.
or Maxwell’s law

\[ \dot{\gamma} = \frac{\dot{\tau}}{G} + \frac{\tau}{\mu} \]  

(14)

where \( \tau = \frac{d\tau}{dt} \).

There are also some fluids which start to flow only after the shearing stress has reached a certain value \( \tau \) called yield stresses. At \( \tau \leq \tau_y \) the fluid is only deformed under the action of the pressure applied; it does not flow.

At \( \tau \leq \tau_y \) fluid flow starts. The behavior of such fluids is given by:

- Bingham – Schwedoff’s law

\[ \tau = \tau_y + \mu_b \dot{\gamma}, \]  

(15)

if the behavior is linear;

- Herschel – Bulkley’s law

\[ \tau = \tau_y + K \cdot \dot{\gamma}^n, \]  

(16)

if the behavior is nonlinear. In relations (15) and (16) \( \tau_y, \mu_b, K \) and \( n \) are material constants.

In the case of electrical circuits, generally, one resorts to Ohm’s linear law (9) and seldom to the nonlinear law (10).

In classical Thermodynamics one uses a nonlinear law, the law of perfect gases where one of its general forms (11) or (12); it refers only to the volume deformation of the gas.

Energy - an unitary concept for description of processes in gases, liquids and solids

Although the behavior of gases, liquids and solids is expressed in a different way, with different concepts, their unitary treatment of processes is possible if we use the concepts introduced by the First Law of Thermodynamics (the quantitative conservation and qualitative non conservation of energy [3; 5]): Work, Heat and Internal Energy.

Energy is a state property; while Heat and Work are process quantities (exchanged energies), which depend on process specificities, or the path to be followed. Thus, Work is energy exchanged in the mechanical interaction between the system and surroundings (in the time of the process), while Heat is the thermal interaction between the system and surroundings.

In its mathematical expression, the spatial loading state of a material body features the stress tensor \( \tau \) and the strain tensor \( \varepsilon \), in the case of solid bodies and the velocity gradient tensor respectively, \( \nabla \dot{v} \) with fluid flow.

One uses the general notation for tensors, \( T_{ij} \) which may be any of the tensors \( \tau_{ij}, \varepsilon_{ij} \) and \( \nabla \dot{v} \).

Each of these tensors is decomposed into a spherical tensor, \( T_{ij}^{(0)} \) and a deviator tensor \( \overline{T}_{ij} \)

\[ T_{ij} = T_{ij}^{(0)} + \overline{T}_{ij}, \]  

(17)

or, generally,

\[
\begin{pmatrix}
\tau_{11} & \tau_{12} & \tau_{13} \\
\tau_{21} & \tau_{22} & \tau_{23} \\
\tau_{31} & \tau_{32} & \tau_{33}
\end{pmatrix}
= \begin{pmatrix}
T_{11} & 0 & 0 \\
0 & T_{22} & 0 \\
0 & 0 & T_{33}
\end{pmatrix}
+ \begin{pmatrix}
T_{11} - T_{12} & T_{12} & T_{13} \\
T_{21} & T_{22} - T_{12} & T_{23} \\
T_{31} & T_{32} & T_{33} - T_{12}
\end{pmatrix}
\]

where:

\[ T_m = (T_{11} + T_{22} + T_{33}) / 3 \]

is the average value of stresses across the main diagonal of tensor \( T_{ij} \).

The spherical stress tensor features the average stress on its main diagonal, while the strain spherical tensor has the average strain on its main diagonal. The action of \( T_{ij}^{(0)} \) results in the body volume deformation, featuring \( \overline{e}_{ij}^{(0)} \).

The relation between tensors \( \tau_{ij} \) and \( e_{ij} \) expresses the matter behavior (solid, liquid or gas), in a deformation process,

\[ \tau_{ij} = F(e_{ij}). \]  

(18)

The relation between \( T_{ij}^{(0)} \) and \( \overline{e}_{ij}^{(0)} \) shows the behavior of matter under the action of volume variation,

\[ \tau_{ij}^{(0)} = F^{(0)}(\overline{e}_{ij}^{(0)}). \]  

(19)

The deviator of stress tensor, \( \overline{\tau}_{ij} \), contains terms whose action upon a solid body produce its variation in shape, given by the terms of the strain deviator, \( \overline{e}_{ij} \). The relation between the two tensor deviators, \( \overline{\tau}_{ij} \) and \( \overline{e}_{ij} \), express the behavior law of the solid material in the case of its shape variation,

\[ \overline{\tau}_{ij} = F(\overline{e}_{ij}). \]  

(20)

In the case of a fluid, the action of the stress deviator tensor components \( \tau \) result in the components of the deviator of velocity gradient tensor or rate of strain deviator, \( \overline{d}_{ij} \). The correlation between \( \overline{\tau}_{ij} \) and \( \overline{d}_{ij} \) case of a certain fluid represents the behavior law of that fluid during its flow,

\[ \overline{\tau}_{ij} = f(\overline{d}_{ij}). \]  

(21)

From a physical point of view the total energy received by a material body from the outside, \( E_t \) is divided into volume variation energy, \( E_v \) and shape variation energy, \( E_s \). Between them there is the relation

\[ E_t = E_v + E_s. \]  

(22)

The terms from relation (22) are functions dependent on the tensors which characterize them. For example, in a pure deformation process (flow free),

\[
\begin{align*}
E_v &= F_1(\tau; \varepsilon_v); \\
E_s &= F_2(\tau; \varepsilon_s); \\
E_t &= F_3(\tau; \varepsilon_v, \varepsilon_s). \\
\end{align*}
\]  

(23)

In a process of deformation and flow one replaces relation (22) with the relation between the corresponding powers \( \dot{E}_v = dE_v / dt \); \( \dot{E}_s = dE_s / dt \) and \( \dot{E}_t = dE_t / dt \),

\[ \dot{E}_t = \dot{E}_v + \dot{E}_s, \]  

(24)

where:

\[
\begin{align*}
\dot{E}_v &= f_1(\tau; \dot{d}_v); \\
\dot{E}_s &= f_2(\tau; \dot{d}_s); \\
\dot{E}_t &= f_3(\tau; \dot{d}_v, \dot{d}_s). \\
\end{align*}
\]

If the solid body volume deformation is neglected, then \( E_v = 0 \), while if the fluid volume deformation is neglected, then \( E_s = 0 \).

In the case of the linear behavior of a solid body undergoing deformation only, in tensorial expression relations (23) become:

\[ \text{REV. CHIM. (Bucharest) } & \bullet \text{ 64 } \bullet \text{ No. 5 } \bullet \text{ 2013 } \text{ http://www.revistadechimie.ro } 459 \]
With the nonlinear behavior of the body under strain loading, for each kind of energy, one resorts to the general relation

\[ E = \int \tau_{ij} \cdot de_{ij}, \]  

(25)

where \( \tau_{ij} \) as \( e_{ij} \) is replaced with the expression resulting from the behavior law or constitutive equation.

From the Enegronics and Thermodynamic point of view the correlation between the energy introduced (as a cause of the process) into a physical system/body, \( E_a = \text{Action Energy} \), and its energetically effects on the system (\( \Delta U \)) and Surroundings (\( Q_p + W \)) is written as (fig. 1),

\[ E_a = Q + W \cdot \beta_w, \]  

(26)

where:

\[ Q = \Delta U + Q_p, \]  

(27)

\( Q \) is the heat resulting from the external action, \( \Delta U \) – variation of internal energy, \( W \) – work, \( Q_p \) – heat lost to the environment,

\[ \beta_w = \begin{cases} 
1, & \text{if the system/body produces work;} \\
-1, & \text{if the system/body receives work.}
\end{cases} \]

From relations (26) and (27) one gets

\[ E_a = Q_p = \Delta U + W \cdot \beta_w. \]  

(28)

Relation (28) can be generalized to be written as

\[ \sum(E_a \cdot \beta_i) - Q_p = \Delta U + W \cdot \beta_w, \]  

(29)

where:

\[ \beta_e = \begin{cases} 
1, & \text{if the system/body receives energy;} \\
-1, & \text{if the system/body give off energy.}
\end{cases} \]

Action Energy \( E_a \) may be: electrical energy, external work, external heat received by the system etc.

Relation (29) is written in the spirit of Energonics [3] and it represents the general principle of conservation of energy written in a new format.

If the body exchanges only heat then one may write

\[ \sum(\Delta E_a \cdot \beta_e) - Q_p = \dot{Q} \cdot \beta_e \]  

(30)

where \( \beta_e = \begin{cases} 
1, & \text{if the system/body receives heat from surroundings;} \\
-1, & \text{if the system/body give heat to the surroundings.}
\end{cases} \)

From relations (28) and (30) one obtains a particular format of general relation (29), which, with \( \beta_0 = \beta_w = 1 \), is the mathematical expression of the principle of conservation of energy expressed in the manner of the first classical format of Thermodynamics (introduced for the first time by Clausius in 1850):

\[ Q = \Delta U + W. \]  

(31)

Let us analyze the content of relation (29) in some scientific chapters, in the particular case where \( i = 1 \):

- in the Theory of Elasticity and in the Strength of Materials, where – in general – one neglects the thermal effects, the internal energy variation caused by volume variation and shape variation \( \Delta U_v = \Delta U_s = 0 \), so that

\[ E_a = W, \]  

(32)

where \( W \) is caused by volume and shape variation

\[ W = W_v + W_s. \]  

(33)

Since in solid deformation, one often considers that with a constant volume, the volume variation is null \( (W_v = 0) \), so that consequently \( W = W_s \) and \( E_a = W_s \).

- in Fluid Mechanics one generally neglects the volume variation, so that \( W_v = 0 \). Then, when one also neglects the thermal effects, so that in relation (29), after derivation with respect to time, it becomes

\[ \dot{E}_a = \frac{dW_s}{dt}; \]  

(34)

- in Rheology and Viscoelasticity, often \( \Delta U_v \approx 0 \) so that,

\[ E_a = \Delta U_s \]  

or

\[ E_a = W_v + E_s \]  

(35)

where \( E_s \) is the energy consumed for the shape variation.

- in Electrodynamics, \( E_a = Q + W_m \),

where \( E_a \) is electrical energy supplied to the conductor; \( Q \) – heat resulting from the passage of the electric current through the conductor; \( W_m \) – work induced by the magnetic field created by the circulation of the electric current of intensity \( I \).

**Energy, Work and Heat in gases**

**Work and Heat in perfect gases processes**

Expressions for \( Q \) and \( W \) depends on the behavior of the gas under load and the specifics of the process involving the gas.

The behavior law of ideal or perfect gases in a polytropic process is given by relation (11) on the basis on which one can write,

\[ p = p_1 \cdot \left( \frac{V_1}{V} \right)^{\gamma}, \]  

(36)

In a process where the gas can pass from parameters \( p_1, V_1 \) to parameters \( p_2, V_2 \) thermodynamic work is written as
wherefrom, after integration, one gets formulas (38) for \( n \neq 1 \) and (39) for \( n = 1 \) (table 2).

If for the perfect gas behavior instead of relation (11) one uses the law written as (12), one gets \([6; 7]\) the formulas (40) and (41) in table 2.

Work corresponding to each physical process which a perfect gas undergoes depends on the initial and final parameters of the gas and on exponent \( n \neq 1 \) from the law of behavior, except the isothermal process.

The heat amount \( Q \) exchanged with the environment in a process where the gas state parameters change from set \( p_1; V_1; T_1 \) to set \( p_2; V_2; T_2 \) is given by relation

\[
Q = W \frac{c_p}{c_v} (T_2 - T_1),
\]

or, after integration,

\[
Q = m \frac{c_p}{c_v} (T_2 - T_1),
\]

where \( c_p \) is the average polytropic specific heat in the temperature interval \( T_1 ... T_2 \) of the gas.

The law of energy conservation under thermodynamic expression (31) in the case of \( \beta = 1 \), for polytrophic processes, leads to relation [6]:

\[
Q = \frac{k - n}{k - 1} W,
\]

where \( k \) is the adiabatic exponent. It follows from relation (44) that thermodynamic work and thermodynamic heat in a polytropic process are correlated by means of the behavior exponents.

The type of process involving the perfect gas is individualized through the value of the polytropic exponent \( n \):

\[
\begin{align*}
    n & = 0 \quad \text{– isobaric process;} \\
    n & = 1 \quad \text{– isothermal process;} \\
    n & = \text{ polytropic process;} \\
    k & = \text{ adiabatic process;} \\
    \pm \infty & = \text{ isometric process.}
\end{align*}
\]

\[
\begin{align*}
    p & = \text{ isotherm}, \\
    n & = k \\
    \text{ polytrop} \\
    \text{ adiabat}
\end{align*}
\]

In diagram \( p - V \) the curve describing a polytropic process is located between the curves corresponding to the isothermal and adiabatic processes (fig. 2) because \( 1 < n < k \).

What is the meaning of the areas of the surfaces between the curves in figure 2? In order to answer this question, let us assume that there are three identical physical systems, undergoing the same amount of energy \( E_a \) (fig. 3).

\[
\begin{align*}
    \Delta V_{p, is} & = 0 \quad \Delta V_{p, pt} = 0 \quad \Delta V_{p, ad} = 0 \\
    W_{p, is} & = 0 \quad W_{p, pt} \neq 0 \quad W_{p, ad} = 0 \\
    Q_{p, is} & = 0 \quad Q_{p, pt} \neq 0 \quad Q_{p, ad} = 0
\end{align*}
\]

Fig. 3. Energetically Effects of the same amount of the Action Energy \( E_a \) upon the same physical system, in different conditions: isothermal (a), polytropic (b) and adiabatic (c)

From the Law of Energy Conservation in its general form (29), or particular form (28), one gets (fig. 3),

\[
E_a = \begin{cases} 
W_p + Q_{p, pt} & \text{– in the case of isothermal processes;} \\
\Delta U_p + Q_{p, pt} + W_p & \text{– in the case of polytropic processes;} \\
\Delta U_{ad} + W_{ad} & \text{– in the case of adiabatic processes,}
\end{cases}
\]

where the indices are to be read as: is – isothermal; pt – polytropic and ad – adiabatic.

From relations (26) written for the three cases from figure 4 in the case of \( Q_{p, is} = 0 \) one gets:

\[
E_a = Q_{p, pt} + W_p = Q_{p, pt} + W_{ad},
\]

where we wrote: \( Q_{p, pt} = \Delta U_{p} \) and \( Q_{p, pt} = \Delta U_{ad} \).

In the adiabatic process (fig. 5, c) the amount of heat \( Q \) may result, for example, from the combustion of a fuel (heat engine) or from a resistor with a current inside, located inside the physical system under consideration. If the volume variation \( \Delta V = 0 \) results \( E_a = \Delta U_{ad} \) on the energy and \( \Delta V = 0 \).

The area under each the curve from figure 4 represents the work of an isothermal, polytropic and adiabatic process, respectively:

\[
\begin{align*}
    \Delta V_{p, is} & = 0 \quad \Delta V_{p, pt} = 0 \quad \Delta V_{p, ad} = 0 \\
    W_{p, is} & = 0 \quad W_{p, pt} \neq 0 \quad W_{p, ad} = 0 \\
    Q_{p, is} & = 0 \quad Q_{p, pt} \neq 0 \quad Q_{p, ad} = 0
\end{align*}
\]

\[
\begin{align*}
    \Delta V_{p, is} & = 0 \quad \Delta V_{p, pt} = 0 \quad \Delta V_{p, ad} = 0 \\
    W_{p, is} & = 0 \quad W_{p, pt} \neq 0 \quad W_{p, ad} = 0 \\
    Q_{p, is} & = 0 \quad Q_{p, pt} \neq 0 \quad Q_{p, ad} = 0
\end{align*}
\]

\[
\begin{align*}
    \Delta V_{p, is} & = 0 \quad \Delta V_{p, pt} = 0 \quad \Delta V_{p, ad} = 0 \\
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\end{align*}
\]

\[
\begin{align*}
    \Delta V_{p, is} & = 0 \quad \Delta V_{p, pt} = 0 \quad \Delta V_{p, ad} = 0 \\
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    Q_{p, is} & = 0 \quad Q_{p, pt} \neq 0 \quad Q_{p, ad} = 0
\end{align*}
\]

\[
\begin{align*}
    \Delta V_{p, is} & = 0 \quad \Delta V_{p, pt} = 0 \quad \Delta V_{p, ad} = 0 \\
    W_{p, is} & = 0 \quad W_{p, pt} \neq 0 \quad W_{p, ad} = 0 \\
    Q_{p, is} & = 0 \quad Q_{p, pt} \neq 0 \quad Q_{p, ad} = 0
\end{align*}
\]
Area $\text{ABB}_1 \text{A}_1 = W_{\text{is}}$; Area $\text{ACB}_1 \text{A}_1 = W_{\text{pt}}$; Area $\text{ABD}_1 \text{A}_1 = W_{\text{ad}}$.

On the other side,

$$
\begin{align*}
\text{DW}_w &= \text{Area ABCA} = \Delta U_{\text{ad}} + Q_{p,pt} - \text{a part of external energy } E_a, \text{ which produces, in the polytropic process, changes of the internal energy, and heat lost to the environment;} \\
\text{DW}_{p-a} &= \text{Area ACDA} = \Delta U_{\text{pt}} - \text{a part of external energy } E_a, \text{ which produces the difference between the adiabatic and polytropic internal energy.}
\end{align*}
$$

Fig. 5. Effects of the same amount of heat received, $Q$, in the same physical system under isothermal (a), polytropic (b) and adiabatic (c) conditions

Forming the ratio $\eta_p = \frac{W_{\text{pt}}}{W_{p,pt}}$ we get

$$
\eta_p = \left\{ \begin{array}{ll}
\frac{W_u}{E_a} = 1 & \text{in an isothermal process without heat losses (where } Q_{p,pt} = 0); \\
1 - \frac{Q_{p,pt}}{E_a} & \text{in an isothermal process with heat losses}; \\
1 - \frac{(\Delta U_{\text{ad}} + Q_{p,pt})/E_a}{1} & \text{in a polytropic process}; \\
1 - \frac{(\Delta U_{\text{pt}}/E_a)}{1} & \text{in an adiabatic process}.
\end{array} \right.
$$

One may write:

$$
\begin{align*}
\text{DW}_{w-p} &= W_u - W_{p,pt} = \Delta U_{\text{pt}} + Q_{p,pt} \\
\text{DW}_{w-a} &= W_u - W_{ad} = \Delta U_{\text{ad}} \\
\text{DW}_{p-a} &= W_{p,pt} - W_{ad} = \text{DW}_{w-p} - \text{DW}_{w-a}.
\end{align*}
$$

From relations (45) and (49, a) we get $\eta_{p,pt} > \eta_{p,ad} > \eta_{p,ad}$.

**Work and Heat in perfect gases in the case of real irreversible processes**

We have to use the new equations form Thermodynamics with Finite Speed [8-17] (TFS), in order to describe the real irreversible processes, with finite speed of the piston $w$. Ideal gases.

Describing the behavior of these systems in the $p$ - $V$ and/or $T$ - $V$ diagram need also the utilization of these new formulae and new concepts [17].

For example for, the adiabatic irreversible process with finite piston speed $w$, M. Paul [18] have proposed in 1937 the following formula (deduced based on kinetico-molecular considerations):

$$
T \cdot V^{\nu-\frac{1}{\nu}} = \text{constant,}
$$

or

$$
p \cdot V^{\nu} \cdot \alpha_w = \text{constant,}
$$

where

$$
\nu = \left\{ \begin{array}{ll}
1, & \text{for adiabatic irreversible compression process of the ideal gas;} \\
-1, & \text{for adiabatic irreversible expansion process of the ideal gas.}
\end{array} \right.
$$

Much later, starting with 1964, L. Stoicescu and S. Petrescu [8, 16, 17] has got similar equations for irreversible adiabatic processes, but with another mathematical format

$$
T \cdot V^{\nu-\frac{1}{\nu}} \alpha_w = \text{constant,}
$$

or

$$
p \cdot V^\nu \alpha_w = \text{constant,}
$$

where

$$
\alpha_w = \left( \frac{1}{a} \right)^2 \frac{\alpha_w}{c - \alpha_w},
$$

with $\alpha_w = \frac{k}{\text{C}_w}$, where $k = \text{C}_w / \text{C}_p$ with $\text{C}_w$ and $\text{C}_p$ - specific heats at constant pressure and at constant volume.

First Law of Thermodynamics for irreversible Processes with Finite Speed $w$ is expressed as...
\[ dU = \delta Q - \delta W_{\text{rev}} \]  
\[ \text{(51, b)} \]

which looks similar with the reversible one \( dU = \delta Q - \delta W_{\text{rev}} = \delta Q - \delta p \cdot dV \), but here (in 51, b) the irreversible work \( \delta W_{\text{irr}} \) has another equation, which is different in comparison with the reversible elementary work \( \delta W_{\text{rev}} = p \cdot dV \), namely \[ \delta W_{\text{irr}} = p_m \left( 1 + \frac{aw}{c} \right) \cdot dV = p_m \cdot dV \]  
\[ \text{(52)} \]

where \( c = \sqrt{3R \cdot T_i} \) and \( p_m \) the average instantaneously pressure in the gas which for a cylinder with a piston is different in comparison with the pressure on the piston \( p_i \). During an expansion process \( p_i > p_m \), but during a compression process the opposite is happening. \( p_i < p_m \).

In the new \( p \cdot V \) diagrams two different curves appear instead of one. An "asymmetry" between compression curve and expansion curve (which describes the process) takes place. The term \( (aw/c) \) is the cause of irreversibility.

A synthesis of the main formulae regarding the computations on Processes with Finite Speed, \( w \), is presented in the table 3.

With these formulae we can now compute any irreversible cycle in a similar way how we did, for reversible cycle, with the only difference that for each irreversible process, we have to use "corrected formulae" which takes into account the cause of irreversibility, namely the finite speed, \( w \). We start with the data in initial state 1 \( (p_1, V_1, T_1) \), and proceed to compute the second state 2 \( (p_2, V_2, T_2) \) knowing what kind of process takes place between these two states. After we have the properties in the second state 2 we compute the work \( W_{12} \) and heat \( Q_{12} \), exactly how we did for reversible cycles, but now using the "corrected formulae" from the table 3, for corresponding irreversible process. For example if the process 1-2 is isothermal, we will use the formula,

\[ W_{12,\text{f}} = Q_{12,\text{f}} = a_w \cdot W_{12,\text{rev}}, \]

with \( c_i = \sqrt{3R T_i} \), where \( T_i = T_2 \).

If the process 1-2 is adiabatic we will use for determining the properties in the second state 2 the corresponding corrected equations from table 3. After we have the properties in the state 2 \( (p_2, V_2, T_2) \) we compute the work and heat in this process with the "corrected formulae".

For heat, there is no difference in comparison with reversible adiabatic process, because the same definition of irreversible adiabatic process, namely \( Q_{12} = 0 \).

But for the work it will appear a difference, which at the first site could be confusing. Looking in the table 3, we "discover with surprise" that the formula for irreversible work \( W_{12,\text{f}} \) is "identical" with the one for reversible work. Actually, despite the same mathematical structure of the formula, we have to remember that the temperature in the point 2, in the case of irreversible process, \( T_{12,\text{f}} \) is different in comparison with the temperature at point 2 in the case of reversible process, \( T_{12,\text{r}} \). We do compute \( T_{12,\text{f}} \) with the new formulae for adiabatic irreversible processes with finite speed written in table 3, depending if we know the volumetric compression ratio \( V_1/V_2 \), if we have as data the pressures compression ratio \( p_1/p_2 \).

S. Petrescu et. al. [10 – 13; 17], extended the formula (52) for more complex irreversible processes

\[ \delta W_{\text{irr}} = p_m \left( 1 + \frac{aw}{c} \cdot \delta_w + \frac{\Delta p_i}{2 p_m} \cdot \delta_w + \frac{\Delta p_f}{p_m} \right) \cdot dV \]  
\[ \text{(53)} \]

where in addition to the first cause of irreversibility \( (aw/c) \) two new causes of irreversibilities were added: throttling \((\Delta p_i)\) and friction \((\Delta p_f)\) pressure drops.

The relationship (53) is the basis of the Thermodynamic with Finite Speed (TFS) and led to invention of the Direct Method of cyclic processes study [11 - 17; 19].

The direct Method consists in the evaluation of irreversibilities of real thermal machine, for each process in the cycle obtaining expressions for the Efficiency and Power as a function of the speed of the process \([8 – 11; 20]\). TFS takes into account both causes of irreversibilities: internal and external, expressed all of them as function of the speed \( w \) in the fundamental equation (53).

The process degree of irreversibility can be calculated based on irreversible work with relationship [3; 21],

\[ \varepsilon_{irr} = \frac{W_{12}}{E_a} \]  
\[ \text{(54)} \]

where \( W \) depends on:
- process speed both in ideal processes as well as in real ones;
- direction of process development for real processes \( (\delta) \).

The process efficiency \( \eta_{w} \) and the degree of irreversibility are complementary and are correlated through relationship [3],

\[ \eta_{w} + \varepsilon_{irr} = 1. \]  
\[ \text{(55)} \]

Relationships of the form (50) where the effect of process development speed is introduced at exponent level \( (1) \), resemble to relationships for action energy participation introduced by the principle of critical energy [21; 22] from Energonics [3], where the influence of the speed of the loading process (static, rapid, shock, a.s.o.) is shown through the exponent value in the specific energy participation expression.

For example, for matter behavior described by the power-law function (3), the participation corresponding to loading with stress \( \sigma \) has the expression [23],

\[ P(\sigma) = \left( \frac{\sigma}{\sigma_{cr}} \right)^{-\alpha}, \]

where \( \alpha = 1/k \) depends on the loading speed, while \( \sigma_{cr} \) is critical stress. In a first approximation [24;25],

\[ \alpha = \begin{cases} 
1/k & \text{at static loading;} \\
1/2k & \text{at rapid loading;} \\
0 & \text{at shock loading.}
\end{cases} \]

The loading is considered (Fig. 6):
- static \((OA_1)\), if \( t/t_p > 3 \);
- rapid \((OA_2)\), if \( 0.5 < t/t_p < 3 \);
- shock \((OA_3)\), if \( t/t_p < 0.5 \),

where \( t \) is the duration for stress increase from zero to \( \sigma \), while \( t_p \) – the period of self-vibration of the loaded element.

Fig. 6. The loading characteristic (I – static; II – rapid; III – shock), function of rationalized duration \( t/t_p \) of stress variation from zero to \( \sigma \).
A more precise evaluation of loading speed influence can be done only if one can express the dependence of \( \alpha \) on the loading speed, \( \sigma = \frac{d\sigma}{dt} \) through a continuous function. This is an open issue. The work and heat analysis in the case of real gases flow, taking into consideration the real irreversible processes, can improve the overall efficiency of the process equipment [26].

Numerical examples

A volume of air is compressed from parameters \( p_1 = 10^5 \) Pa, \( T_1 = 293 \) K and \( V_1 = 0.5 \) m\(^3\) to parameters \( p_2, T_2 \) and \( V_2 = 0.05 \) m\(^3\) (fig. 2).

It is considered that air in the processes of volume deformation behaves like an ideal gas (11). Exponents from ideal gases law (11) have the following values:

\[ n = 1.20 \quad \text{for a polytropic process;} \]
\[ n = 1.4 \quad \text{for an adiabatic process.} \]

Compression ratio

\[ \frac{V_2}{V_1} = 10. \]

a. Calculate the mechanical work in the reversible processes, polytropic, adiabatic and isotherm. The mechanical work is calculated with the relationships,

\[ (W_{12})_p = \frac{p_1 \cdot V_1}{n-1} \left[ 1 - \left( \frac{V_2}{V_1} \right)^{n-1} \right] = 10^5 \times 0.5 \times \frac{1}{1.2-1} \left[ 1 - (10)^{1.2-1} \right] = 1.462 \times 10^3 \text{ J} \quad \text{polytropic process;} \]

\[ (W_{12})_ad = \frac{p_1 \cdot V_1}{k-1} \left[ 1 - \left( \frac{V_2}{V_1} \right)^{k-1} \right] = 10^5 \times 0.5 \times \frac{1}{1.4-1} \left[ 1 - (10)^{1.4-1} \right] = 1.89 \times 10^3 \text{ J} \quad \text{adiabatic process;} \]

\[ (W_{12})_i = p_1 \cdot V_1 \cdot \ln \left( \frac{V_2}{V_1} \right) = 10^5 \times 0.5 \times \ln(0.1) = -1.1513 \times 10^3 \text{ J} \quad \text{isotherm process.} \]

b. Calculate the mechanical work at compression in an irreversible adiabatic process, if the compression of air is made in a cylinder with piston, whose average speed is \( \omega = 15 \) m/s.

The behavior law (50) is used. The mechanical work of the irreversible compression process results from the second relationship (38) through the replacement of \( n \) with \( \frac{n}{i} \).

\[ (W_{12})_{irrev} = \frac{p_1 \cdot V_1}{n \cdot i - 1} \left[ \left( \frac{V_1}{V_2} \right)^{n-i} - 1 \right], \]

where \( i \) is calculated with relationship (50, a).

Air is characterized by

\[ c = \sqrt{3R \cdot T} = \sqrt{3 \times 284.045 \times 323} = 524.633 \frac{\text{m}}{\text{s}}, \]

where \( R = \frac{8.314}{M} \) Pa m\(^3\)/kmol °C, with \( M = 29.27 \) kg/kmol is the molecular weight of air. For the beginning one chooses \( T = 323 \) K – average temperature of air. Consequently, with \( \delta = 1 \) (compression),

\[ (W_{12})_{irrev} = \frac{p_1 \cdot V_1}{n \cdot i - 1} \left[ \left( \frac{V_1}{V_2} \right)^{n-i} - 1 \right] = \left[ \left( \frac{V_1}{V_2} \right)^{1-1} - 1 \right] = -1.462 \times 10^3 \text{ J} \]
The final temperature of gas is calculated with the first relationship (50)

\[ T_2 = T_1 \cdot \left( \frac{V_1}{V_2} \right)^{1/\gamma} = 293 \times \left( \frac{1.0}{0.1} \right)^{1/1.4} = 790 \text{ K} \]

The average temperature of gas is

\[ T = 0.5(T_1 + T_2) = 0.5(293 + 790) = 541.5 \text{ K} \]

It results \( c = \sqrt{3R \cdot \bar{T}} = \sqrt{3 \times 284.045 \times 293} = 679.287 \text{ m/s} \).

One calculates again \( i_w \) and results:

\[ i_w = 1 + 2.60067 \frac{w}{c} \cdot \delta_w + 3 \cdot \frac{w^2}{c^2} + 3.6743 \frac{w^3}{c^3} \cdot \delta_w = 1.057375 \]

With \( n=k=1.4 \), results – in a first approximation – irreversible adiabatic mechanical work,

\[ (W_{12})_{ad, prev} = \frac{p_1 V_1}{k \cdot i_w - 1} \left[ 1 - \left( \frac{V_1}{V_2} \right)^{(n-1)/n} \right] = \frac{10^5 \times 0.5}{1.4 \times 1.057375 - 1} \left[ 1 - (10)^{1.4 \times 1.4 \times 0.057375 - 1} \right] = -210.5 \text{ kJ} \]

It resulted in absolute value

\[ |(W_{12})_{ad, prev}| = 210.5 \text{ kJ} > |(W_{12})_{ad, irr}| = |(W_{12})_{ad}| = 189 \text{ kJ} \]

\[ c. \text{ Solving case } b \text{ based on law (51) and relationships in table 3.} \]

The calculation of irreversible adiabatic mechanical work based on law (51), using relationship (52), is done similarly to those presented in case \( b \).

For example, when using relationships (51, a) and (52), with

\[ \alpha_w = \left(1 + \frac{a \cdot w}{c} \cdot \delta_w \right)^2 = \left(1 + 2.0494 \times \frac{5}{152.93} \right)^2 = 1.1385 \text{ (compression)} \]

and \( a = \sqrt{3 \cdot k} = \sqrt{3 \times 1.4} = 2.0494 \);

\[ \alpha_n = \left(1 + \frac{a \cdot w}{c_1} \cdot \delta_n \right)^2 = \left(1 + \frac{2.0494 \times 15}{499.67} \right)^2 = 1.1268 \];

\[ \alpha_{n_2} = \left(1 + \frac{a \cdot w}{c_2} \cdot \delta_n \right)^2 = \left(1 + 744.236 \right)^2 = 1.0843 \],

where \( c_1 = \sqrt{3R \cdot T_1} = \sqrt{3 \times 284.045 \times 293} = 499.67 \text{ m/s} \);

\[ c_2 = \sqrt{3R \cdot T_2} = \sqrt{3 \times 284.045 \times 650} = 744.236 \text{ m/s} \],

where it was chosen, in a first approximation, \( T_2 = 650 \text{ K} \).

One recalculates

\[ T_2 = T_1 \cdot \left( \frac{V_1}{V_2} \right)^{1/\gamma} \left( \frac{\alpha_n}{\alpha_{n_2}} \right)^{1/\gamma} = 293 \times (10)^{1.1268} \times 1.0843 = 764.83 \text{ K} \);

\[ c_2 = \sqrt{3R \cdot T_2} = \sqrt{3 \times 284.045 \times 750.274} = 799.584 \text{ m/s} \]

\[ \alpha_n = \left(1 + \frac{2.0494 \times 15}{799.584} \right)^2 = 1.0784 \]

\[ T_2 = 293 \times (10)^{1.1268} \times 1.0784 = 769 \text{ K}. \]
The adiabatic mechanical work, in the irreversible process of compression, has the expression from table 3

$$\left( W_{12}\right) _{ad,irev}=-\frac{p_1 V_1-p_2 V_2}{k-1} = 10^5 \times 0.5 - 26.246 \times 10^5 \times 0.05 = -203.075 \times 10^5 J,$$

where

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right)^{\frac{\alpha_1}{\alpha_2}} = 10^5 \times \left( \frac{1.1268}{1.0784} \right) = 26.246 \times 10^5 Pa.$$  

In absolute value

$$\left| (W_{12})_{ad,irev} \right| = 203.075 \text{ kJ} > \left| (W_{12})_{ad,rev} \right| = 189 \text{ kJ}$$

One notices that the mechanical work in the irreversible adiabatic process calculated with the two methods has approximately the same values; both resulted values are greater than the mechanical work in the reversible process.

![Fig. 7. Adiabatic compression with finite speed, $w$, in the case of reversible (1) and irreversible process (2).](image)

The two adiabatic compression processes, reversible and irreversible, are presented in figure 7. The difference of mechanical work in the two cases (irreversible – reversible) is

$$DW_{rev-rev}=(W_{12})_{ad,rev}-(W_{12})_{ad,rev} = \begin{cases} 
-203.075 - (-189) = -7 \text{ kJ} & \text{for behavior law Petrescu (51);} \\
-210.5 - (-189) = -14.075 \text{ kJ} & \text{for behavior law Paul (50);}
\end{cases}$$

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