FROM THERMOKINETICS – TO THE ENERGODYNAMICS

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The author generalizes thermodynamics of irreversible processes on processes of useful transformation of energy in thermal and not thermal, cyclic and not cyclic engines. For this purpose it suggests to find thermodynamic forces $\mathbf{X}_i$ and flows $\mathbf{J}_i$ from the energy conservation law, but not "entropy production". Further it opens indissoluble communication of processes of transfer and transformation of any forms of energy, unity of their laws and existence for them antisymmetric reciprocal relations, confirming their fairness on a wide class of the processes, submitting to Maxwell's equations.

Introduction.

The growing comprehension of the fundamental role the rate and productivity play in real processes as one of the basic indices of their efficiency gave rise to two new branches in thermodynamics of the XX century called thermodynamics of irreversible processes (TIP) [1…10] and finite-time thermodynamics [11…16] respectively. The first of the branches involves time as physical parameter introduced into the thermodynamic equations and a new macrophysical method developed on this basis for investigating kinetics of interrelated transfer phenomena. This branch has enriched the theoretical conception of the XX century with a number of new principles of general-physics meaning (including those of linearity, reciprocity, minimal entropy generation) and evidently contributed into cognition of the in-depth interrelations between dissimilar phenomena. However, TIP basing on the entropy rise law is restricted to investigating *dissipative processes* such as thermal conduction, electrical conduction, diffusion, as well as effects of their superposition, but has nothing to do with the issues of *productivity of useful conversion processes* which are the principal object of thermodynamics. As a result, the broadest spectrum of irreversible processes with a relative efficiency above zero appeared to have fallen beyond cognizance of this theory.

The second branch, on the contrary, sets as a top-priority task the definition of the conditions to achieve maximum *useful* of cyclic heat engines with due consideration given to the irreversibility of heat exchange processes and finite-time contact between a working media and heat wells and sinks. Within the frames of this theory the problem has been posed for the first time and in the most general form about the relation between the capacity (productivity) of engineering systems and their thermodynamic efficiency, as well as about the critical capabilities of irreversible processes. However, this theory in its existing configuration is restricted to units wherein the operation at maximum power conditions is economically most advantageous. Though the spectrum of such units is broad enough (includes nuclear power plants, renewable plants, space vehicle power plants, etc), it does not include a number of power and process units wherein maximum of their efficiency does not correspond to maximum power. In this context a necessity arises to synthesize the said branches and create on this basis a unitary theory of rate and productivity pertaining to transfer and conversion processes, which would cover the entire spectrum of real processes and occupy the same position relative to the classic theory of heat engines as dynamics to statics. We have named the theory of such type as *Thermokinetics* [17].

However and Thermokinetics is limited by processes, connected with the thermal form of energy. In the mean time processes of transfer and transformation of energy interest not only power engineering wherein these processes are principle. The thermodynamic investigation of biological systems is also impossible without catering for work supporting the non-equilibrium state of such systems and providing their vital activity [18]. The application of thermodynamics to cosmological objects that develop, according to current ideas, bypassing equilibrium would also be incomplete without work considered as ordered form of exchange. This refers to also antirelaxation phenomena observed under regular conditions at superposition of dissimilar irreversible processes (superposed when running simultaneously in the same spatial areas) and studied by synergetics [19]. In this context there is an indispensability of the further generalization of thermokinetics and creations the *energodynamics* as uniform theory of processes of transfer and transformation of any forms of energy irrespective of their accessory to this or that area of knowledge. This theory should supplement thermokinetics with the analysis *of interrelation between efficiency and productivity (net capacity) of various kinds of converters (cyclic and non-cyclic, heat and non-heat).* At its creation we have tried to bring as small as possible corrective in thermokinetics to make its method suitable for research enough wide range of scientific disciplines, processes and systems.

1. The concept of useful internal work against of equilibrium

As we have shown earlier [20], the energy of spatially non-uniform system is function of coordinates of three independent groups of processes: transfer Θ_i, redistribution $\mathbf{r}_i$ and reorientation $\boldsymbol{\varphi}_i$, where $i = 1, 2, \ldots, n$ – number of energy components equal to the maximal number of independent processes for some of their categories. This means that the exact differential of energy $Э$ may be expressed by the following identity:

$$dЭ \equiv \Sigma_i \psi_i \, d\Theta_i - \Sigma_i \mathbf{F}_i \cdot d\mathbf{r}_i - \Sigma_i \mathbf{M}_i \cdot d\boldsymbol{\varphi}_i, \tag{1}$$

where – the total energy of the system; Θ_i – the generalized coordinates of transfer processes (heat exchange, volumetric deformation, mass exchange, electrization, accelerations, etc. (энтропия S, volume V, mass M, a charge $З$, an impulse $\mathbf{P}$, etc.); $\mathbf{r}_i$ – a displacement of the radius-vector of the Θ_i center from its position in equilibrium state; $\boldsymbol{\varphi}_i$ – a deviation of spatial angle of a vector $\mathbf{r}_i$ from equilibrium value; $\psi_i \equiv (\partial Э/\partial \Theta_i)$ – the generalized potentials such absolute temperature T and absolute pressure p, chemical, electric, etc. potential; $\mathbf{F}_i \equiv -(\partial Э/\partial \mathbf{r}_i)$ – forces in their usual (Newtonian) meaning; $\mathbf{M}_i \equiv -(\partial Э/\partial \boldsymbol{\varphi}_i) = \mathbf{F}_i \times \mathbf{R}_i$ – the “torsion” torque is advisable to be called the “orientation” torque in the case it becomes zero when $\boldsymbol{\varphi}_i = 0$ [21].

The fundamental identity of energodynamics (1) thus obtained is valid regardless of what causes the variation of the parameters Θ_i, $\mathbf{r}_i$ and $\boldsymbol{\varphi}_i$ – either the external energy exchange or the internal (including relaxation and anti-relaxation) processes. Last is made against equilibrium in system in processes 'ascending diffusion', active transport in biosystems, polarization of substances, self-organizing of systems, etc. Therefore (1) is applicable to *any processes* (both reversible and irreversible). At the same time it is most detailed of all the relationships connecting the parameters of spatially heterogeneous systems since it allows for *any possible categories of processes* running in such systems [22].

For isolated systems the right-hand member of identity (1) becomes zero. For systems not changing its spatial orientation ($\boldsymbol{\varphi}_i =$ const) the two last terms in (1) may be combined, then the fundamental identity of energodynamics becomes:

$$dЭ \equiv \Sigma_i \psi_i \, d\Theta_i - \Sigma_i \mathbf{F}_i \cdot d\mathbf{r}_i. \tag{2}$$

To clarify the meaning of the terms of the second sum in (1), we must take into account that they correspond to the redistribution processes running at constant parameters Θ_i and $\boldsymbol{\varphi}_i$, i.e. with invariable direction of the unit vector $\mathbf{r}_i$. Then $(\partial Э/\partial \mathbf{Z}_i) \equiv -\mathbf{X}_i = \Theta_i^{-1}(\partial Э/\partial \mathbf{r}_i) = -\mathbf{F}_i/\Theta_i$, then the $\mathbf{X}_i$ ‘*thermodynamic forces’* thus introduced are actually the specific forces in their usual (Newtonian) meaning, i.e. the forces $\mathbf{F}_i$ per unit of the value Θi they transfer [22].

Using them enables representation of work by two equivalent expressions:

$$\text{đ}W_i = \mathbf{F}_i \cdot d\mathbf{r}_i = \mathbf{X}_i \cdot d\mathbf{Z}_i. \qquad (3)$$

The work described by expression (2) may be external or internal (depending on where the forces arise – either in the system itself or outside); useful or dissipative (depending on what the work involves – either purposeful conversion of energy or its dissipation); long – range or short–range (depending on radius of action); mechanical, thermal, electrical, chemical, etc (depending on nature of the forces to overcome).

At the same time the energodynamics emphasizes a fundamental difference between *ordered* $\text{đ}W_i^{\text{т}} = \mathbf{F}_i \cdot d\mathbf{r}_i$ and *unordered* $\text{đ}W_i^{\text{н}} = \psi_i d\Theta_i$ works described by 1-st and 2-nd sum of the equation (1). Their fundamental difference consists not only by the variables of scalar and vector character. This distinction consists that work of type $\text{đ}W_i^{\text{н}} = \psi_i d\Theta_i$ is a quantitative measure of process of transfer of energy while work $\text{đ}W_i^{\text{т}} = \mathbf{F}_i \cdot d\mathbf{r}_i$ – a quantitative measure of process of its transformation [23]. This difference is kept and at concept of work on the scalar form. If a system is heterogeneous, i.e. $\mathbf{X}_i = -\nabla\psi_i \neq 0$ and $d\mathbf{Z}_i = \Theta_i d\mathbf{r}_i \neq 0$, then

$$\text{đ}W_i^{\text{т}} = \mathbf{X}_i \cdot d\mathbf{Z}_i = -\Theta_i\,(d\mathbf{r}_i \cdot \nabla)\psi_i = -\Theta_i d\psi_i, \qquad (4)$$

where ψ_i is the potential of some part in the heterogeneous system, which varies with part-to-part transfer within the system, i.e. should be considered as a function of system position $\mathbf{r}_i$ in the field of the ψ_i potential. Thus the terms $\mathbf{X}_i \cdot d\mathbf{Z}_i$ describe the *i*th energy form variations caused by the above redistribution of the energy carrier Θ_i if kept in the system as a whole. In accordance with the energy conservation law this is possible only as a result of other energy forms converted into the i^{th} form. Therefore ordered work is always associated with the *energy conversion* process. The undertaken expansion of the space of variables by introducing the vectors of displacement $\mathbf{r}_i$ makes it possible to cover not only quantitative, but as well *qualitative* variations of energy in various forms. The fact that *vector processes* run in systems along with *scalar processes* means that both the *ordered* are generally done in such systems.

Due to the fact that energodynamics rejects in its grounds the process idealization expressed in such notions as “quasi-static” (infinitely slow), “equilibrium” and “reversible” a possibility appears to introduce time as a logically consistent physical parameter into its equations. For that it is enough to rewrite identity (1) in the form containing total derivatives of the state parameters earlier introduced with respect to time *t*:

$$d\text{Э}/dt \equiv \Sigma_i\ \psi_i d\Theta_i/dt - \Sigma_i \mathbf{F}_i \cdot \mathbf{v}_i - \Sigma_i\ \mathbf{M}_i \cdot \boldsymbol{\omega}_i. \qquad (5)$$

Here $\mathbf{v}_i \equiv d\mathbf{r}_i/dt = \mathbf{e}_i dr_i/dt$ – translation velocity of the energy carrier Θ_i ($\mathbf{e}_i = \mathbf{r}_i/r_i$); $\boldsymbol{\omega}_i \equiv d\boldsymbol{\varphi}_i/dt$ – angular velocity of its reorientation (or rotation). In the particular case, when the parameter Θ_i means mass of a system, the values $\mathbf{v}$ and $\boldsymbol{\omega}$ characterize its linear and angular velocity as a whole.

The relationship thus obtained between the local variables the field theories operate with and the thermodynamic parameters characterizing the state of a continuum in whole opens the possibility of describing their properties from the positions of energodynamics. In this case particular importance is attached to introducing in thermodynamic equations the most significant for natural science in whole concepts of flows $\mathbf{J}_i, \mathbf{j}_i$ as generalized rates of the transfer processes and the concept of power (capacity) of the energy conversion process in a whole system $N_i = \mathbf{X}_i \cdot \mathbf{J}_i$ and in its unit volume $\mathbf{x}_i \cdot \mathbf{j}_i$ [24]. It should be noted that the notion of capacity refers to only the useful energy conversion processes and, therefore, could not appear in the depths of the theory of irreversible processes restricted to consideration of exclusively dissipative phenomena. On the contrary, all basic relationships of this theory will hereinafter be obtained as a consequence from energodynamics.

2. Indissoluble unity of processes of transfer and transformation of energy

Classic thermodynamics, having time excluded from its equations, did not considered the processes of energy and its carriers transfer. Therefore the issue regarding unity of energy transfer and conversion processes could not arise in its depths. *N. Umov* (1873) was the first who paid attention to that relation and stated the energy conservation law for mechanical processes rather as a consequence of energy transfer across the system borders than as a result of energy disappearing in some points of space and appearing in others [25]. It remained unanswered, however, what was the "transfer substrate" in that case – either the material energy carriers attributed to the extensive values Θ_i category or the intensive values ψ_i as analogs of mechanical stresses. Energodynamics gives an answer to this question. According to it the flux of any i^{th} form of energy is expresses as the product of the intensive measure of motion – the generalized potential ψ_i – and the energy carrier flux $\mathbf{J}_i$ that is defined, in its turn, as the product of the extensive measure of motion Θ_i of this particular kind being transferred and the velocity $\mathbf{v}_i$ of its transfer in space. This flux density $\mathbf{j}_i$ is accordingly expressed as the product of the density $\rho_i = \rho\Theta_i$ of this extensive value and its transfer velocity $\mathbf{v}_i$. The transfer concepts extraneous to classic thermodynamics find thereby their realization in energodynamics.

Furthermore, energodynamics allows to consider not only energy interchange between the systems and the environment, but also in relaxation processes running in them, as the displacement vectors $\mathbf{r}_i$. This fact is usually taken into account by the so-called balance equations, which integral form looks like:

$$d\mathbf{r}_i = d_u\mathbf{r}_i + d_r\mathbf{r}_i \,. \tag{6}$$

Here $d_u\mathbf{r}_i$ – similar variations of the $\mathbf{r}_i$ coordinates caused by useful work of the i^{th} kind; $d_r\mathbf{r}_i$ – one-sided spontaneous variations of the same parameters caused by running internal (relaxation) processes and, depending on sign, named usually either "wells" or "sinks" of corresponding parameters. Expression (6) may be more conveniently represented as the flow balance equation:

$$\mathbf{J}_i = -\,\mathbf{J}_i^u + \mathbf{J}_i^r\,;\;\; \mathbf{j}_i = -\,\mathbf{j}_i^u + \mathbf{j}_i^r, \tag{7}$$

where $\mathbf{J}_i^u = -\,d_u\mathbf{r}_i/dt$; $\mathbf{J}_i^r = d_r\mathbf{r}_i/dt$ – useful and relaxation components of the $\mathbf{J}_i$ flow, respectively. Here the positive direction of the flow, just as the forces $\mathbf{F}_i$ and $\mathbf{X}_i$, is construed as the direction toward equilibrium, which corresponds to the rule of signs accepted in thermodynamics, viz. the external work $\mathbf{F}_i{\cdot}d_u\mathbf{r}_i$ is positive if done by a system [26].

Due to the mutual balance between the wells and the sinks of various coordinates energodynamic identity (1) remains valid even when the variation of its terms is caused by internal (irreversible) processes. In other words, the thermodynamic identity *remains valid within the entire spectrum of real processes* – from "quasi-reversible" to maximum irreversible. Besides it facilitates distinguishing between the energy *transfer* processes (within the same form) and the energy *conversion* processes (from some form into another). The terms of this sum may be endued with a more conventional form if taking into consideration that the redistribution processes correspond to the expansion of $\nabla{\cdot}(\psi_i\mathbf{j}_i^u)$ given that $\nabla{\cdot}\mathbf{j}_i^u = 0$. For the system as a whole this condition becomes $\int\nabla{\cdot}\mathbf{j}_i^u\, dV = 0$. Changing in this expression from the space integral to the integral $\int\mathbf{j}_i^u{\cdot}\boldsymbol{n}\, df = 0$ taken through the closed surface f of the system gives that at $\mathbf{j}_i^u \neq 0$ the said condition indicates the parts f' and f'' existing on this surface with the opposite sign of the $\mathbf{j}_i^u{\cdot}\mathbf{n}$ product, i.e. the flows $\mathbf{j}_i'$ and $\mathbf{j}_i''$ existing as entering the system and leaving it, respectively. In this case

$$\int\mathbf{j}_i{\cdot}\mathbf{n}\, df = \int\mathbf{j}_i'{\cdot}\mathbf{n}\, df' + \int\mathbf{j}_i''{\cdot}\mathbf{n}\, df'' = J_i'' - J_i' = 0, \tag{8}$$

where $J_i' = \int\mathbf{j}_i'{\cdot}\mathbf{n}\, df' \leq 0$ and $J_i'' = \int\mathbf{j}_i''{\cdot}\mathbf{n}\, df'' \geq 0$ – flows (flow rates) of energy carrier at the system input and output, respectively.

Thus in balance equation (7) the external component of the flow $\mathbf{J}_i^u$ caused by the useful external work W_i^{T} done may be distinguished from the relaxation component $\mathbf{J}_i^r$ by the conservation of the energy carrier flow rates J_i' and J_i'' at the system input and output. Representing in (7) the bulk element dV covered by the flow $\mathbf{j}_i^u$ as a product of its cross section vector element $d\mathbf{f}$ normal to the flow and the normal element $d\mathbf{n}$ ($dV = d\mathbf{f} \cdot d\mathbf{n}$) and also considering that in a steady flow $(d\mathbf{n} \cdot \nabla)\psi_i = d\psi_i$ one may derive instead of the addend in (8):

$$N_i = \int\left(\int \mathbf{j}_i^u \cdot d\mathbf{f}\right) d\psi_i = -\int J_i^u d\psi_i = J_i^u\,(\psi_i' - \psi_i''), \tag{9}$$

where $J_i^u = -\int \mathbf{j}_i^u \cdot d\mathbf{f} = J_i'' = -|\,\mathbf{J}_i'|$ – external "transit" flow of energy carrier crossing the system and remaining unvaried in value; ψ_i', ψ_i'' – input and output potentials of energy carrier, respectively.

Thus the useful component is associated with the "transit" flow of energy carrier J_i^u which crosses the system with its value invariable. This statement may be instantiated by an electric machine where the input current is known to be equal to the output one. This is equally evident for a cyclic heat engine, too, since in any cycle the entropy rise with the heat supply $\Delta S_{1\text{-}2}$ in process 1-2 is numerically equal to the entropy decline $\Delta S_{2\text{-}1}$ process 2-1 with the heat rejected to heat sink. Therefore, at steady conditions the entropy flow rates $J_s^u = \Delta S/\Delta t$ at the system input and output are as well equal. This is the circumstance that was foundational for S. Carnot to compare heat engine with a mill-wheel (hydraulic machine).

As follows from the aforementioned, the condition necessary to provide the conversion of some i^{th} energy form consists in the availability within the energy converting system an adequate energy carrier flow J_i^u crossing the areas with a various value of the generalized potential Ψ_{i}. For heat engines this is the entropy flow J_s^u from heat well with a temperature of T' to heat sink with a temperature of T''; for electric machines – the electric current J_e^u associated with the electric potential differential $\Delta\varphi$; for concentration elements – the substance flow J_k^u crossing the borders of a system with different values of chemical potential; for mechanical engines – the gas or liquid flow between the zones with different values of enthalpy or pressure, etc. This distinguishing feature of the energy conversion processes, viz. transfer of a corresponding thermostatic value Θ_i in the field of the X_i forces, is characteristic for micro-heterogeneous systems, too. In fact, a flow proper of some value across the borders of a system implies there are "flow-out" and "flow-into" zones in the system, i.e. subsystems reversing their properties in the course of energy conversion. These may be electrons and "holes" in semiconductors, positive and negative ions in electrolytes, opposite charges or poles of electric and magnetic dipoles, bulk elements shifting in opposite directions in bodies under deformation, etc. [26].

This means that any system taking part in energy conversion process (either a source of technically fit energy, or the converting device proper, or the work object, or whatever else) should always be considered as an extended (heterogeneous) system, which different parts reverse their state. Such state variations are, in the broadest sense, that "compensation" for the energy conversion process, which necessity R. Clausius advocated.

Expression (9) is valid for both the i^{th} (being converted) and the j^{th} (having been converted) forms of energy. This means that any energy converting device (both cyclic and non-cyclic) is a system "transfused" with the energy-carrier flows of both "being-converted" $\mathbf{J}_{\mathrm{i}}$ and "having-been-converted" J_{j} forms of energy. Such a "two-flow" system in electrical engineering is represented as a "four-terminal" network in electrical engineering and radio-engineering, i.e. a device with two pairs of input and output terminals. For clearness, an electrical "equivalent circuit" to an energy converting device is shown in Fig.1.

The energy converting device depicted on this figure (central part) looks like being "transfused" with two different-kind flows of the energy carriers $\mathbf{J}_i$ and $\mathbf{J}_j$. It is emphasized thereby that this device interacts with not just one, but two objects – *the source of technically fit energy* and *the work object.* The principal distinction of a four-terminal network from the heat engine concept adopted in thermostatics as a set of heat well, working medium and heat sink is that the energy converting device (working medium analog) in the four-terminal network contacts two “extended” systems, each being non-equilibrium and including energy carrier wells and sinks (similar to the extended system). The function of the energy converting device in such a circuit is using the spatial heterogeneity in some material objects in order to create an artificial heterogeneity in other ones (work object).

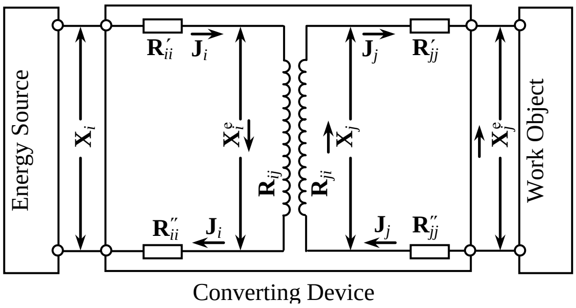

Fig.1. Electrical Equivalent Circuit to energy Converting Device

The functional division of the material objects participating in the energy conversion process stresses the *inseparable unity of the energy transfer and conversion processes* and provides the necessary generality in posing the issue on the thermodynamic perfection of the energy conversion process in heat and non-heat, cyclic and non-cyclic engines [27].

Such an approach is extremely important since the wells and the sinks of whatever source of energy can not be distinguished in nature with the same easiness as the heat wells and heat sinks. It is very difficult to distinguish the energy wells and sinks in such media as, e.g. homogeneous chemically reacting mixture, polarized or magnetized media, dissociated gases, deformed elastic bodies, etc. Nevertheless, those are known to be able to do useful work like the discontinuous systems. Sensing them as a non-equilibrium single whole promotes the formation of a correct world outlook and the comprehension that all man-used energy sources, without exception, ultimately belong to only the environment and are caused by environmental spatial heterogeneity. This implies not just a possibility, but also an inevitability of using the environmental energy. The apparent contradiction of this conclusion with classic thermodynamics (its second law) that excludes the usage of the environmental heat is caused by just the fact that classic thermodynamics interprets the environment simplistically as something homogeneous. It is this environment that embodies the Ostvald-proposed concept of perpetual motion of the second kind as a heat engine using the practically inexhaustible heat well of the world ocean. Now, when power installations exist using the temperature difference between the surface and subsurface oceanic layers, i.e. the part of this indeed inexhaustible heat well, the narrowness of equilibrium thermodynamics in posing problems and drawing conclusions is undeniable.

3. Unity of any forms of energy transformation laws

The necessity to have both wells and sinks of entropy, charge, substance, momentum, etc. ensuing from (9) once again emphasizes the flexibility of the law of excluded perpetual motion of the second kind. This statement results in a possibility for each of the energy converting devices to be estimated by the process power N_i related to the energy flow at the inlet to the energy converter J_e':

$$\eta_i = N_i / J_e' = N_i = 1 - \bar{\psi}''_i / \bar{\psi}'_i, \tag{10}$$

where $\bar{\psi}'_i$, $\bar{\psi}''_i$ – mean-integral values of the generalized potential at the device inlet and outlet.

This index refers to the so-called “absolute efficiencies” class. According to this expression the absolute efficiency characterizes the convertibility degree of the energy supplied from some energy well. This degree is defined by exclusively the relation between the mean values of a corresponding generalized potential and, providing this relation is constant, does not depend on the working medium properties, design and other characteristics of the energy converting system. Since energy wells with a potential of $\bar{\psi}_i' = \infty$ or energy sinks with a potential of $\bar{\psi}_i'' = 0$ are physically unfeasible, the 100% absolute efficiency is unattainable in even reversible processes. This verdict generalizes the Carnot theorem known for ideal heat engines confirming once again the conclusion that the laws of heat conversion stated by thermodynamics are just a particular case of the universal laws of nature valid for any forms of energy.

Let us now show that expression (10) is valid for cyclic heat engines, too. To do so, let us interrelate the so-called "mean-thermodynamic" temperatures $\bar{T}_1$ and $\bar{T}_2$ in the heat absorption and rejection processes with the mean-integral temperatures T_s' and T_s'' of entropy flows at the device inlet and outlet. If ΔS_1 and ΔS_2 characterize the variations of the working medium entropy with the heats absorption and rejection Q_1 and Q_2 in some cycle, while Δt_1 and Δt_2 – duration of these processes, then the total flows of heat J_q' and J_q'' and entropy J_s' and J_s'' will be defined as:

$$J_q' = Q_1 / \Delta t_1 \,;\; J_q'' = Q_2 / \Delta t_2 \,; \tag{11}$$

$$J_s' = \Delta S_1 / \Delta t_1 \,;\; J_s'' = \Delta S_2 / \Delta t_2 \,. \tag{12}$$

Considering the relationship between the flows of heat and entropy as $J_q = T_s J_s$ gives:

$$\bar{T}_1 = Q_1 / \Delta S_1 = J_q'/J_s' = T_s' \,, \tag{13}$$

$$\bar{T}_2 = Q_2 / \Delta S_2 = J_q''/J_s'' = T_s''. \tag{14}$$

The identity of the temperatures averaged over the time of heat supply to the working medium in a heat exchanger to the temperatures averaged over the heat exchange surface allows deriving the thermal efficiency of an arbitrary cycle in terms of the heat flow parameters:

$$\eta_t = 1 - Q_2 / Q_1 = 1 - T_2 / T_1 = 1 - \bar{T}_s''/\bar{T}_s'. \tag{15}$$

Then

$$J_s' = J_q'/T_s' = J_s'' = J_q''/ T_s'' \,. \tag{16}$$

Thus marking the border of the energy converting device along the surface of heat exchange with the heat well and heat sink the operation of the cyclic heat engine may be reduced to the operation of a direct-heat-conversion machine with the same theoretical power N^u:

$$N^u = J_q'\eta_t = J_s' \,(T_s' - T_s'') = J_s'\Delta T_s, \tag{17}$$

where $\Delta T_s = T_s' - T_s''$ – motive force of the heat transfer and conversion process defined by the energy well and sink parameters.

The unified expression of absolute efficiencies for heat and non-heat, cyclic and non-cyclic engines (10) shows that this value depends on neither a kind of the energy being converted and design of the energy converting device, nor on its working medium nature or parameters. Therefore the value η_i, as well as η_t, strictly speaking should not at all be termed as "engine efficiency". This value is defined by exclusively the parameters of the "hot" and "cold" energy well on the border with the working medium, i.e. by the energy flow parameters, but not the properties of the engine as itself. In other words, the "absolute efficiencies", including the "thermal", "internal", "effective", "electrical", "enthalpy", etc. efficiencies widely used in analysis of heat power units characterize rather the capabilities provided by nature due to its intrinsic spatial heterogeneity in dispensing of whatever intensive property. These efficiencies characterize just the maximal "convertibility degree" of a particular energy form, which is attained in the same machine with the quasi-static nature of the processes involved therein (when all the processes are "reversible").

According to the Carnot theorem this efficiency does not depend anymore on the working medium properties within the energy converting device, i.e. relates to some abstract (idealized) machine naturally not occurring. Since all reversible processes are infinitely slow running, the power of such a machine is infinitesimal. Therefore in energodynamics dealing with real processes and machines we will be avoiding to apply the term “efficiency” to the value η_i terming it rather “energy convertibility degree”.

The so-called “relative” efficiencies have other meaning. In classic thermodynamics this notion is introduced in order to estimate the perfection of particular processes in heat power engines, e.g. the working medium expansion processes. Such efficiencies mean the work W_i^{T} actually done in the process related to its theoretically possible value W_i [28]. These are the efficiencies (relative) all other disciplines operate except thermodynamics. For non-cyclic machines doing one kind of the useful work these efficiencies actually characterize the perfection degree of a machine (i.e. the losses therein). The fact that thermodynamics operates absolute efficiencies, whereas the other disciplines operate relative ones, has caused confusion time after time. Quite often lamentations have been raised for a low efficiency of heat power stations and up-to-60%-of-fuel heat “wasted” to the environment, whereas the efficiency of fuel cells, electric and many other machines reaches 90% and above. But for all that it has never occurred to the “complainants” that only several percents of the Q_2 heat given away in excess of a certain minimum of Q_{2t} can be referred to the so-called “wasted heat loss” since the heat Q_{2t} is not a loss, but the *condition necessary to provide the energy conversion process as itself.*

To eliminate this misconception and provide a methodologically unified approach to the converters of any forms of energy, the concept of relative efficiency should be generalized to all kinds of the energy converting devices. To this end let us consider the power ratio between the converter inlet N_j and outlet N_i :

$$\eta_N = N_j/N_i = X_j J_j^{\mathrm{e}}/X_i J_i^{\mathrm{e}} \leq 1 . \tag{18}$$

This expression is quite close by implication to the notion of relative internal efficiency of heat engines in classic thermodynamics and goes over into it after multiplication of the numerator and denominator in (9) by an arbitrary time span Δt. In this case the (9) numerator characterizes the useful work actually done by the machine $W_i = X_j J_j^{e} \Delta t$, while the denominator – its theoretically possible value $W_i^{\mathrm{T}} = X_i J_i^{u} \Delta t$. We will be terming the (9) ratio a “power” efficiency of the energy converting device. It is this expression that ensues from the law of energy conservation in the form $N_i = \mathbf{X}_i \cdot \mathbf{J}_i$ for a particular case of a single-target machine intended for the conversion if the i^{th} form of energy into the j^{th} one.

Let us show now that it is this efficiency that characterizes the thermodynamic perfection of a machine, i.e. the degree the machine implements those potentials the well of the technically adequate (ordered) energy provides for it. In fact, according to the principle of heat and work equivalency the ordered work W^{T} done by a cyclic machine related to the algebraic sum of the heats $đQ$ it receives at all stages of the cyclic process is always equal to unity. Relating this work to only that part of the heat Q_1 which is taken from the “hot” well is, from a mathematical standpoint, an implicit technique, moreover, such one that is not always feasible for even the heat engines (in particular, for the processes where temperature rise cohabits with heat rejection). This even more concerns the non-heat engines where the energy wells and sinks occupies the same space (such are, in particular, polarized, magnetized, etc. bodies). At such conditions it is advisable to consider only the actual power of the machine N_j related to that theoretically possible; such a ratio being construed as the power efficiency.

Another advantage of the power efficiency lies in its applicability to the analysis of multi-functional machines implementing a simultaneous conversion of several kinds of energy. Further advantage of the power efficiency is its applicability to the same extent to both the direct cycles and the reverse ones, for which the relative efficiency loses its meaning because the power consumed in this process is more than theoretically required. Ultimately the power efficiency application makes machines more compatible in the degree of perfection of the processes running therein since it allows for losses of all kinds – both at the energy transfer from the well to the converting device and at the energy conversion in the device itself.

To show the non-triviality of this concept, let us compare the η_N with the so-called "*exergy efficiency of technical systems for energy and substance conversion*" η_{ex} [29]. The latter characterizes the ratio of outlet exergy flow to inlet exergy flow in the machine. For an "extended system" (as including wells and sinks of heat, substance, charge, etc.) the exergy becomes its state function. The exergy flows are equidimensional with power, which links the exergy and power efficiencies. However, the exergy efficiency is not always associated with the conversion of some kind of energy into other one due to the so-called "transit" exergy flows existing. Such is, e.g. the exergy of flow of some substance crossing the reactor and not participating in the chemical transformations therein. Therefore the exergy flow ratio does not yet characterize the effectiveness of the energy conversion in a machine. Besides, the exergy efficiency depends on the exergy value itself as it is commonly construed, i.e. on the reference point choice for some form of exergy or other. This makes the exergy efficiency ambiguous, which restricts the applicability of this working capability function in the efficiency analysis for power and process installations [30].

Representing the power efficiency in terms of the flows J_i^u and J_j^u referring exclusively to the energy conversion processes eliminates the shortcomings of the exergy efficiency. The further consideration will confirm the power efficiency is the concept that not only corresponds to its physical meaning, but also provides the most objective assessment of the thermodynamic effectiveness of any energy converters [31].

4. Antisymmetry of reciprocal Relation of «energytransformation» Processes

As is known, in L. Onsager postulated that for minor deviation from thermodynamic equilibrium any of the flows J_i obeyed the law of linear dependence on all the thermodynamic forces X_j active in the system [32]:

$$J_i = \Sigma_j L_{ij} X_j . \quad (i,j = 1, 2, \ldots, n) . \tag{19}$$

Onsager referred to those laws of relaxation processes, as well as the associated coefficients L_{ij}, as "phenomenological" (i.e. practicebased). The off-diagonal summands in expression (20) were introduced by Onsager to allow for various "superposition" (interrelation) effects of processes running simultaneously in the same spatial zones.

The most important in the Onsager's theory was proof of reciprocity relationships between the "off-diagonal" phenomenological coefficients [33]:

$$L_{ij} = L_{ji} . \ (i \neq j) \tag{20}$$

These symmetry conditions reduce the number of the coefficients L_{ij} to be experimentally defined from n (for mere empirical description) down to $n(n+1)/2$ (where n – a number of independent flows).[1] After Onsager, H. Cazimir [34] extended the Onsager's theory to cover vector processes, having herein proved that in case the α and β-type forces (even and odd time functions) acted simultaneously, the reciprocity relationships (20) would go over into the anti–symmetry conditions:

$$L_{ij} = - L_{ji} \tag{21}$$

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[1] L. Onsager was afterward awarded the Nobel Prize (1968) for his studies in that field.

One can make sure such an interrelation exists if compare, based on the law of conservation of energy, the expressions of the energy being converted and having been converted:

$$N_i = N_i^r + N_i^u = N_j^{\,r} + N_j^u. \tag{22}$$

This relationship is an equation of balance between the power input to the machine and power output from the machine. According to this equation the power input N_i is consumed to overcome both the subscript-similar dissipation forces X_i and the “alien” forces X_j, i.e. is not only converted into other form of the useful energy N_i^u, but also partly dissipates on the input resistors (this loss is usually designated as N_i^r). In its turn, the power N_j converted into the jth form is also partly lost in the secondary equivalent circuit (Fig.1) thereby reducing the output useful power N_j^u necessary to overcome the useful forces X_j^u. Since by the law of conservation of energy

$$N_i^u = X_i J_i^u = N_j^u = X_j J_j^u, \tag{23}$$

the flows J_i^u and J_j^u appears to be interrelated. This interrelation shows itself in the fact that each of the flows J_i and J_j appears to be dependant on both the active forces X_i and X_j acting in the system, i.e. the kinetic equations of the energy conversion process should be written a priori in the form of Onsager’s phenomenological laws:

$$J_i^{\mathrm{r}} = L_{ij} X_i + L_{ij} X_j\,, \tag{24}$$

$$J_j^{\mathrm{r}} = L_{ji} X_i + L_{jj} X_j\,. \tag{25}$$

The number of the phenomenological coefficients in these equations may be reduced by applying the reciprocity relationships to them. However, it is advisable to preliminarily make sure the reciprocity relationships for the energy useful conversion processes bear invariably antisymmetrical character [35]. To this end let us take into account the difference in sign for the work done to the energy converting device (this work is negative according to the rule of signs in thermodynamics, i.e. $\text{đ}W_i^{\mathrm{T}} = -X_i dZ_i < 0$) and the work done by this device to the work object $\text{đ}W_j^{\mathrm{T}} = X_j dZ_j > 0$. With the sign properly considered the exact differential of system energy may be expressed as

$$d\text{Э} = X_i dZ_i - X_j dZ_j\,. \tag{26}$$

From here on the basis of the known theorem of independence of the second derivative of the system energy Э with respect to the coordinates Z_i and Z_j follows:

$$(\partial X_i/\partial Z_j) = (\partial X_j/\partial Z_i). \tag{27}$$

As $dZ_i = J_i dt$ and $dZ_j = J_j dt$, after reduction dt it is had:

$$(\partial J_i /\partial X_j) = -(\partial J_j/\partial X_i). \tag{28}$$

This proof of the so-called Cazimir’s reciprocity relationships differs from those earlier proposed [36] by a particular simplicity and obviousness. The opposite sign of the works $\text{đ}W_i$ and $\text{đ}W_j$ taken into account results in kinetic equations (25), (26) taking the form:

$$J_i^u = L_{ij} X_i - L_{ji} X_j\,, \tag{29}$$

$$J_j^u = L_{ji} X_i - L_{jj} X_j\,. \tag{30}$$

The kinetic equations of such a character (with their terms having different signs) correspond to the concept of phenomenological (experience-based) laws than initial equations (25)–(26).

The primary energy carrier flow J_i (e.g. the current in the primary winding of a transformer) is commonly known to decrease as the forces X_j being overcome increase (with approach to "no-load" operation) or, on the contrary, to increase as these forces decrease (with approach to "short circuit" operation). Similarly, the secondary energy carrier flow (e.g. the current in the secondary winding of a transformer) is commonly known to increase as the supply voltage X_i increases and to decrease as the secondary circuit resistance and the X_j decrease.

The proof of the Cazimir's reciprocity relationships adduced here for reversible part of the energy conversion processes is based on the law of energy conservation and, therefore, valid whenever linear phenomenological laws (29) and (30) remain valid. This circumstance throws fresh light on the origin of the Cazimir's reciprocity relationships $L_{ij} = -L_{ji}$ exposing the underneath meaning of the requirements for different parity of forces with respect to time inversion. In fact, for the dissipation forces not changing their signs with time inversion (i.e. for the so-called "α-type forces") the Onsager's symmetry conditions $L_{ij} = L_{ji}$, as shown above, are valid. Whenever a part of these forces have the reversible character (i.e. refer to the "β-type forces"), the Onsager's reciprocity relationships give place to anti-symmetry conditions $L_{ij} = -L_{ji}$. At the same time the consideration endeavored here shows that the applicability of the Cazimir's relationships is not actually restricted to the different-parity forces (α and β-type) case. In fact, let us assume dealing with energy conversion processes of purely dissipative character. Such are, in particular, thermal conductivity, electric conductivity, diffusion and viscous friction described by Fourier's, Ohm's, Fick's and Newton's laws and resulting in only the substance and energy transfer. In this case all terms of kinetic equation (19) describing vector phenomena have the same sign $X_i \cdot J_i > 0$ defined by their contribution to dissipative function. In this case reciprocity relationships (20) defining value and sign of the phenomenological coefficients L_{ij} in linear kinetic equations (19) give invariably positive values of the phenomenological coefficients $L_{ij} > 0$ in these equations and result in Onsager's reciprocity relationships $L_{ij} = L_{ji}$.

So for linear transfer processes of a purely dissipative character the matrix of phenomenological coefficients is always symmetrical. However, if in a transfer process useful (reversible) energy conversions occur, i.e. work is done against whatever forces other than dissipation ones, the reciprocity relationships acquire other character. In this case phenomena of the "ascending diffusion" type (transfer of components toward their concentration increase), system ordering, etc. are observed. These processes lead to gradients or differences of temperature, pressure, concentration, electric potential, etc., i.e. to deviation of the system from the internal equilibrium state for some of its degrees of freedom, whereas the system in whole is tending toward equilibrium. As a matter of fact, this is the nature of all the so-called "superposition effects" the theory of irreversible processes deals with. As we will make sure hereafter, the effects of such a kind bear anti-dissipative character. The processes of useful conversion of the i^{th} form of energy into the j^{th} one in various machines apply to these effects, too. This substantially extends the applicability of the anti-symmetrical reciprocity relationships [36].

It is a matter of interest to confirm the anti-symmetrical reciprocity relationships (27) on a wide class of the processes, submitting to the Maxwell's equations. For this let us consider a system consisting of a closed electric circuit with an arbitrary length ℓ_e and variable (in general case) cross section f_e, which comprises an as well closed magnetic circuit with a length ℓ_m and cross section f_m variable thru the length. In this case in the equation (26) X_i and X_j represent accordingly electromotive $X_e = \int \mathbf{E} \cdot d\boldsymbol{\ell}_e$ and magnetomotive $X_M = \int \mathbf{H} \cdot d\boldsymbol{\ell}_M$ forces, while $J_e = dZ_e/dt = \int (d\mathbf{D}/dt) d\mathbf{f}_e$, $J_M = dZ_M/dt = \int (d\mathbf{B}/dt) d\mathbf{f}_M$ – total fluxes of electric and magnetic displacements, respectively, sometimes named the "linkage fluxes" and traditionally represented by the number of the lines of force linking the cross section of the electric and magnetic circuits, respectively [37]. Here **E, H** – electric and magnetic fields; **D, B** – vectors of electric and magnetic induction.

Let us now change, based on the Stokes theorem, in the force equation $X_e = \int \mathbf{E} \cdot d\boldsymbol{\ell}_e$ from the curvilinear integral taken over the closed electric circuit with a length of ℓ_e to the integral $\int \mathrm{rot}\mathbf{E} \cdot d\mathbf{f}_M$ over the magnetic circuit cross section f_M. In the similar way one can change in the force equation $X_M = \int \mathbf{H} \cdot d\boldsymbol{\ell}_M$ from the curvilinear integral over the closed magnetic circuit with a length of $\ell_М$ to the integral $\int \mathrm{rot}\mathbf{H}\cdot d\mathbf{f}\mathrm{e}$ over the surface f_e covering the electric circuit. Then $\partial X_e/\partial \mathbf{f}_М = \mathrm{rot}\mathbf{E}$; $\partial X_М/\partial \mathbf{f}_e = \mathrm{rot}\mathbf{H}$; $\partial^2 Z_e/\partial \mathbf{f}_e \partial t = \partial J_e/\partial \mathbf{f}_e = d\mathbf{D}/dt$, and $\partial^2 Z_М/\partial \mathbf{f}_М \partial t = \partial J_М/\partial \mathbf{f}_e = d\mathbf{B}/dt$. Substituting these expressions in reciprocity relations (28), we shall find:

$$\mathrm{rot}\ \mathbf{E} = -\, d\mathbf{B}/dt, \tag{31}$$

$$\mathrm{rot}\ \mathbf{H} = d\mathbf{D}/dt. \tag{32}$$

These equations differ from the corresponding Maxwell's equations in that they contain the total time derivatives of electric and magnetic induction vectors. This is not a surprise since the primary equations of energodynamics as well contain the exact differentials of polarization and magnetization vectors (K. Polivanov, 1982). To form equations (31) and (32) into a more habitual type, we shall consider, that $d\mathbf{D}/dt = \mathbf{j}_e + (\partial \mathbf{D}/\partial t)>$ where $\mathbf{j}_e = \varrho_e \mathbf{v} = (\mathbf{v}\cdot\nabla)\mathbf{D}$ – conduction current caused by the free charge transfer, whereas magnetic analogs to the free charge ρ_e do not exist and $d\mathbf{B}/dt = (\partial \mathbf{B}/\partial t)$. Thus finally:

$$\mathrm{rot}\ \mathbf{E} = -\,(\partial \mathbf{B}/\partial t); \tag{33}$$

$$\mathrm{rot}\ \mathbf{H} = \mathbf{j}_e + (\partial \mathbf{D}/\partial t); \tag{34}$$

$$\mathrm{div}\ \mathbf{D} = \rho_e\ ; \tag{35}$$

$$\mathrm{div}\ \mathbf{B} = 0\ . \tag{36}$$

Except for that, the differential relationships between the state parameters and their functions enable solution of also other problems. In particular, they allow calculating by experimental data the fundamental state functions of a system. Although these relationships can not describe the mechanism of processes under investigation, they impose the restricting conditions that should be met for each of models. This always clarifies the models because allows neglecting redundant or non-existent constraints. Therefore, the differential relationships are a very effective tooling of mathematical analysis conducted on an object of investigation [38].

As we see, the energodynamics generalizes the methods of thermokinetics to the processes of useful conversion of energy in any forms and irrespectively of the field of knowledge they belong to.

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