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On the boundaries of deterministic description of real heat processes in classical thermodynamics and on their expansion in quantum thermodynamics

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Initial principles Carnot's theory of heat engines are discussed. The interpretation of kay notions of this theory and the boundaries of the description of nonequilibrium to wit real processes in classical thermodynamics based on energy conservation law on exact data Joule's calorimetry are refinement. The causes and the conditions of the irreversibility when thermodynamically description of the nonequilibrium intensive processes, which lead to entropy increment of real systems, are analyzed. The consistency and more completeness of the description of such nonequilibrium processes is given in the frame of deterministic of *energy and entropy conservation laws* in *quantum thermodynamics.* Characteristic for its principle in the form of self-oscillatory quantization is grounded on the unattanaibility of local thermodynamic equilibrium (LTE) in nonequilibrium systems owing to of difference rates of the proceeding in their of elementary relaxation processes. Quantum – thermodynamic effects of intensive heat processes in real systems are allowed for the refinement of their actual local temperature.

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1. Initial principles Carnot's theory on motive force of a heat (1824), contemporary their meaning and the tendencies development sufficient in detail are reflected in the books [1-7]. In his "Reflections on driving force of a fire and on the engines can develop this force" [1] Carnot had adhered to *energy conservation law* U in the form of a heat Q and work W, satisfied of the condition of their *reversibility* when real intensity processes and the level of calorimetric measuring at the time. He had considered of the unnecessary to explain "…what is latent a heat ("*chaleur*"), temperature, heat capacity …", their close notions and quantity of a *chaleur* a *calorique*…, using their without the difference as sorts of a heat, but was logical in the endowing of the two different shades of the definition of a *chaleur* and a *calorique*, as different of the sorts of weightless substance when the description of *thinkable* circular processes. Thas, thermal state of working substance of heat engines Carnot had defined by a term *chaleur* and when the description of circular process for the extraction a work from a *heat*, to wit of the conversion a heat to work, he used the term *calorique.* But, the shades of a difference of this terms were show when analyze of initial principles of his theory.

The first from such principles is in the form:

"The arising of driving force obliged is not actual of a expense of calorique but its transition from a hot bodies to cold ones, to wit by the re-establishment of its equilibrium,…. which was had disturb of any kind cause, be whether chemical action, as a burning, or anything other,…". And "…a heat can be by the cause of the motion only then, when it stimulate the bodies to change their volume or form; this changes being the result of…just in consequence of variable

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action of a heat and cold; to warm anything body, need to have more warm one, to cool its need to have more cold one".

The second principle: "…everywhere where there is temperature difference, can take place the arising of motive force.Inversely, "everywhere, where can to spend this force, can to create temperature difference…, and disturbed the equilibrium of a calorique".Then "…maximum of motive force is obtaining by the application of a vapor there is also the maximum of motive force is obtaining by any means". And "…necessary condition of the maximum will be in those bodies, used for the development of motive force of a heat it is not be no temperature change, taking place from no change of the volume".

Thus, the first principle Carnot's theory is the receipt in vapor engines of *motive* force of variable action (by the cycles) with the expenditure of energy from external springs, but *only* on the cooling their working substances for the change of their volume or form. The second principle is the creation of sufficient conditions for the reversibility of moving force of vapor or of the other heat engines when temperature difference between their heaters and coolers, and the creation of need condition of maximum efficiency of thus engines is only when the synonymous bond between the temperature and volume their working substances.

That is why by the most important his purpose [1] Carnot considered to study the process of the *motion* of a calorique for the *extraction* from *one* a force (work), independent from a type of heat engines, of some kind of a mechanism their action and working substance. For the solution of this problem it must be to find *force,* as a spring of the *motion*, "slipping away" as a rule in the frames of energy conservation law. But such *force* and its spring Carnot find by intuition in just form of the *calorique,* capable allow for *inertia* changes of the volume or the form of working substances of heat engines, supposing by cyclical their action when as if *spontaneous* the giving of a *chaleur* to the heaters of heat engines without the expense of external forces, as from the spring of infinity great power.

2. The purpose of this work is as much possible the use of the results Carnot's theory of heat processes and its progress in classical thermodynamics. It direct on the consistency and more completeness of the description of real heat nonequilibrium processes in the frame of *quantum thermodynamics*, based on generalized principle of the symmetry of such processes as the combination of *energy and entropy* conservation laws.

For the ground of entropy *conservation* law and generalized of the principle of the symmetry on the whole use most rich in content part Carnot's theory, experimental data classical thermodynamics on the ground of entropy *increment* law, their characteristic critical discussions and modern notions on the use of the quantum theory is not only to the microworld but to the whole physics.

In particular, this paper is co-ordinate with Carnot's notion on the such *quantity symmetry* of heat processes which would be satisfied of energy conservation law, but is not as sum a *heat* Q and *work* W in view mutual independent components, and when their *quality non-equivalence* owing to the difference of the velocities their propagation, as need and sufficient of the conditions of energy directed *motion* by the *portions.* As a result, Carnot's theory of heat processes on yourself his of idea orientation turn out on the level of modern notation on the quantum of action and on discreetness of quantum processes in the thermodynamics, and is not only in quantum mechanics, electrodynamics, statistical physics and others adjacent with their sciences.

From the basis of classical thermodynamics the most attention in the paper directed to critical analyze its the first principle. Though need and sufficient conditions of the maximum efficiency of the action of heat engines, which in classic thermodynamics is not coincide with the notion of the reversibility of heat processes and with energy conservation law in view of caloric equivalence of a and a heat, up to now remain by the object of more deep analyze of initial of this condition.

2.1. The motives of the generalization of energy conservation law in Carnot's theory arise when increase of the *intensity* of heat processes for more total conversion of a heat to a work. Energy conservation law in the electrodynamics and mechanics did not exclude of the possibility its use when statement of phenomenological J. Fourier's law (1822) on the dependency of *steady* heat flux $\boldsymbol{q}$ of low density from temperature gradient ∇T and from heat conductivity coefficient, $\lambda(t)$=const or $\lambda(T,t)$, which in latent form is dependent from the time when weak deviation from the equilibrium, in the equation of heat conduction,

$$\mathbf{q} = -\lambda \nabla T, \qquad \lambda[W/m \cdot degree]. \tag{1}$$

But the description practically of innertionaless flux of electric energy $\boldsymbol{J}$ by the equation in a view (1) with electrical conductivity coefficient $\sigma(t)$, dependent from the time in latent form, when $\partial\sigma(t)/\partial t >> \partial\lambda(t)/\partial t$ and comparable energy of fluxes $\boldsymbol{q}$ and $\boldsymbol{J}$, then limitation $\boldsymbol{J}$ on the deviation from electrodynamical equilibrium is incomparable less relatively one from thermodynamically equilibrium of the flax $\boldsymbol{q}$.

The accounting of the influence of later inequality in the time of the search of optimal models of a heat adequate of steadied processes, be complicated by serious illness Carnot's, which bring to his untimely death (1832). And only after two year of his death and 10 year after the publication Carnot's "Reflections...", his younger contemporary, French engineer and physicist B. Clapeyron, with who Carnot when his life did not associate, for the first time published (1834) the first review on his "Reflections..." in "Memoir on driving force of a fire". In its he recognize, that "his a leading idea... is a fruitful and immaculate" [2]. But when analyze Carnot's circular processes and graphical their image, based on energy model of a heat, without the accounting of difference models *chaleur* and *calorique*, Clapeyron took into account only controlled by hand macroscopic cycles of the heat engines between their of the heaters and coolers when their temperature differences, $T_h - T_c > 0$. Such notation Carnot's cycles in Clapeyron's interpretation leaded to rough approximate formulation for the maximum of the efficiency of heat engines,

$$\eta_{ccl} = 1 - T_c/T_h, \tag{2}$$

achievable only when differentially small of temperature difference, $(T_h - T_c) \to dT$, that limited its practical use even when at *infinite slow* processes and leaded to the need its revision. In particular, in the (1) were not taken account of such high-speed processes as electromagnetic radiation, gravitation, electron emission.

2.2. The beginning of the progress of classical thermodynamics coincide with the formation of generalized model of a heat as energy carrier in a heat processes instead of the two Carnot's models, the chaleur and the calorique. Generalized model of a heat must would be lead to the refinement of the temperature for the expression not only of anthropomorphous shade of qualitative sensations of a heat and a cold [2], but and of the deterioration its equilibrium quantity owing to *steady* non-equilibrium of real systems. The generalization Carnot's theory, dedicated to the conversion of low intensity of a heat Q to a work W in the frame *energy* conservation law, on the processes of any intensity, undoubtedly, require and more general statement of *energy flux* conservation law. But the progress of the thermodynamics of real processes it grew way of the statement of *heat* conservation law and the search of its equality tie with the entropy *S, as* the function of the state of the systems, incrementing in real nonequilibrium processes, leaving of the notations of the temperature in rough approximation of local thermodynamically equilibrium (LTE). One can just on that cause the transition from substantial models (chaleur and calorique) to generalized energetic model without the refinement its definition for the description of real processes, is not lead in spite of the waiting to visible advantages of such theory of nonequilibrium processes in the macroscopic systems.

In the time, after experimental definition of high accuracy by J. Joule [2] on mechanical equivalence of a heat lead R. Clausius's and V. Thomson's (1850 - 51) to the generalization Carnot's energy conservation law in heat processes by *caloric equivalence* of a heat and work. On this base with the replacement substantial models of a heat by generalized energy model of one with the accounting proposed by Thomson of the notation of absolute temperature had formulated the first law (*principle*) of classical thermodynamics,

$$Q = dU + W, \tag{3}$$

where dU is total differential of the element of internal energy U, usually is not satisfied of energy conservation law of real systems owing to dissipation energy Q^R in the environment, expressed by incomplete differentials Q and W. The description of the processes of energy *motion* U from hot bodies to cold ones when temperature difference between ones and the derivations of real systems from LTE in the frames of *second* thermodynamics low lead to the increment of entropy S, as function of state systems, and to the inequality in the form,

$$Q \leq TS, \tag{4}$$

The unification of this two *principles* give main thermodynamic equation [1,2],

$$T \geq dU + W, \tag{5}$$

which expand the limits of the description of heat processes in its but on the cost by the loss of the possibility to show the cause of the transition of a heat from a hot bodies to cold one, which Carnot were use intuitive. Yet, itself fact of equality accounting of such natural effect by the inequalities (4), (5) stimulated the revision of this problem.

2.3. The causes and effects of entropy increment.

Thus, only *caloric* but not more general equivalence a heat and work, as indisputable experimental fact, for Clausius's be devoted to the service of science serve by the only reliable of the argument for that to elucidate the cause of incomplete conversion of a heat to a work when absolute completeness of the reverse of its conversion. Besides, introduced by W. Thomson's of the notation of *absolute* temperature assimilated at the time in more broad essence, to wit as absolute *universal* definition independent from the intensity of studying processes. But just the notation on the asymmetry of a heat processes and on introducing of absolute temperature become by the *causes* of the wordings of energy conservation law (3), as of the firs principle of the thermodynamics and the second its principle, as *fundamental law* of the nature in the form *inequality* (4), but as the consequence of *increment* entropy S on measure of the increase of the intensity of real heat processes.

In spite of seeming on the first look limited the possibilities of classical thermodynamics owing to the wording its the second principle in the form inequality (4), most substantial the part of this principle and main equation (5) of the thermodynamics, as its direct consequence, consist in exceptionally broad region their application in the course of time of more then one and a half century. Just thermodynamics prove to be the sours of many kay directions not only in the physics and technical but in the many adjacent with their sciences, including chemical, biology and even sociology. At the same time, the structure of the expressions (3)-(5) in the form of the inequalities actually little suitable for the description of the transfer a heat Q of high intensity from hot bodies to cold ones and their conversion without energy expenditure from external sources. Moreover, this inequalities is can not indicate on the cause of observed direction of heat processes even when their low intensity.

Deterministic description of the problem of heat conversion Q to a work W in the frames of the principles of classical thermodynamics it is really but when strict observance of *energy conservation law* in heat processes. By the condition of real action of this law apparently is *strict* accounting of dissipation energy Q^R to the environment and latent part of energy, $E^* = W^* \rightarrow Q^*$, inversely and on of well-known experimental data with the *inevitable* of complete of the conversion to a heat Q^*, when energy balance of more complex structure then in classical thermodynamics,

$$W = Q^R + Q^r, \quad Q^r = Q - Q^*. \tag{6}$$

Meanwhile, practical realization of the condition (6), complicated by the need of the accounting of latent part of the energy $E^* = W^*$, reversible converted to a heat Q^*, compensate effect of entropy increment S, at least partly. When such interpretation of real heat processes it is not basis to deep in the details of characteristic for quantum thermodynamics, it is not directed to the study of the details entering in coneptional for its the condition (6) on energy components of nonequilibrium systems but to the refinement in their of energy and entropy conservation laws.

3. Initial positions and principles of quantum thermodynamics.

By main initial positions of quantum thermodynamics take on modern the notation on discrete quantum the character of occurring in the nature of energetic processes. Just is why by the analyzes and refinement of the first principle of classical thermodynamics in this paper is given most the attention. In its is proposed the wording of energy conservation law as the alternative of caloric equivalence a heat and work, which is reduced to the grounded of the in unattainability of local thermodynamic equilibrium (LTE) in real nonequilibrium of heat processes, which compensates in real thermodynamics systems the effect of entropy increment. By direct consequence of the accounting of unattainability LTE of real system become entropy conservation law independent from the intensity occurring in their of heat processes.

The axioms adiabatic and LTE unattainability are not contradict to the entropy increase law but only define more precisely of it and the components of internal energy conservation law of real systems with the indication on it still latent energy source. The first principle of quantum thermodynamics as *internal energy conservation law* of real system, is formulated by the exact equations in the *total differentials.* The second, *independent* from its principle is given *the flow internal energy law* by dint of the choice from the real systems of the *use work* when the unattanaibility of its LTE and the optimization of the control by circular macro processes with the combination of microscopic alternation of the quanta a work and heat.

The principles of quantum thermodynamics defines more precisely and completes of the principals of the classical and nonequilibrium of the thermodynamics, the theory of heat conduction, thermal electron emission and the statistical methods, elaborated by Frenkel [7] and Vlasov [8]. For example, data [7] on the behavior of the entropy of system when the definition of element of phase space Δ ,with the accounting and without the accounting of influence force of interaction between the particles are definition ones. Its showed, that Boatsman H – theorem, proofed for the model of particles as hard elastic spheres, grounded processes satisfied of the entropy increase law. For the estimate influence of the view of interaction potential of atomic particles of real systems on the chance in their of the entropy were used of hard sphere and the electrons with Colombo's interaction potential and propagation function indistinguish between itself particles, $f(r,\ v,\ w,\ \omega,\ldots,\tau)$, which satisfies Vlasov's conservation law in the form [8],

$$\partial f/\partial\tau + div_r vf + div_v wf + div_w \omega f + \ldots = 0, \qquad (7)$$

where $\tau,\ r,\ v,\ w\ldots$ - time, coordinates of particles, their velocities and accelerations of the first order.

In the paper [13] relaxation times on their energy, $\tau_r \equiv \tau_q$, and the impulses, $\tau_r \equiv \tau_p$, at steady heat conduction of monatomic particles estimated with the accounting [9-12] and relaxation equation for the description (Moscow, 1965) of shock waves,

$$dE(\tau)/d\tau = -[E(\tau) - E_\infty]/\tau_r. \qquad (8)$$

The accounting of infrontal mutual collision [13] for the model of sphere gives their of relaxation times,

$$\tau_\varepsilon \approx 4\tau_L, \tau_p \approx 2\sqrt{2}\,\tau_L, \qquad (9)$$

in the $L-$ subsystems with the sizes of order of mean free pats of monoatomic particles in time τ_L. Different value of relaxation parameters leading to the inequality $\tau_L < \tau_p < \tau_\varepsilon$, responsible for local self-oscillations in the $L-$ subsystems and the attainability in their LTE is the condition of partial reversibility of heat microprocess of the same of low rate. Analyze of the process approach to the equilibrium with difference rates by dynamically dependent between itself of such microprocesses within L – subsystem and between the two adjacent L – subsystems on the normal to the isotherms, conform the generation in their of local self-oscillations [14 -17].

4. Conclusion.

By main initial positions of quantum thermodynamics take on modern the notation on discrete quantum the character of the occurring in the nature of energetic processes, which satisfied of energy conservation law.

It is proposed as the alternative of caloric equivalence of a heat and work more rigorous wording of energy conservation law taking into account in real nonequilibrium systems the unattainability of local thermodynamic equilibrium (LTE), which in real of heat processes compensates the effect of entropy increment.

By direct consequence of the accounting of unattainability LTE in real systems become entropy conservation law independent from the intensity occurring in their of heat processes.

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