Part 3

ELIMINATION OF NEGATIVE CONSEQUENCIES OF THERMODYNAMICS EXTRAPOLATION

The permanent merit of the classic thermodynamic method, viz. an immutable validity of its consequences, engenders the investigators' natural desire to apply thermodynamic methods to solution of new problems and, furthermore, to extend these methods to new fields of knowledge not relating to thermodynamics. The main technique used for that is an "adaptation to classic" with the help of various hypotheses, postulates and remote analogs. As a rule, such a technique does not involve attempts to revise and generalize the basic concepts and thermodynamic laws, since specialists are oversensitive in apprehending these attempts. Such extrapolation results in so intricate entwinement of truth and errors that it often is impossible to be untwined due to multiple "metastases" – unforeseen remote consequences. The objective of this Section is to consider from more general positions of energodynamics a number of consequences obtained beyond the applicability of the classic thermodynamics and resulted in a number of paralogisms appeared in it, viz. fallacious statements, though, seemingly, quite credible.

Capter 10

CORRECTION OF THERMODYNAMICS OF OPEN AND POLYVARIANT SYSTEMS

Classic thermodynamics in accordance with the equilibrium self-nondisturbance principle has always excluded from consideration the spontaneous state variations including the internal processes of variation in system composition, structure, chemical properties, etc. There are, mean-

time, chemical thermodynamics, thermodynamics of solutions, phase transitions, etc. We owe such an extension of thermodynamic methods' applicability to J. Gibbs (1875), who replaced the internal irreversible processes by the reversible processes of system–environment exchange of the kth substances. With this purpose in mind he represented non-equilibrium system as a set of equilibrium open subsystems, viz. phases and components exchanging substance with the environment. Thus thermodynamics was supplemented with one more type of the external heat exchange reducible to neither heat, nor work and usually named a diffusion of the kth substances across the system borders[1].

Since the classic thermodynamic methods may be used for studying only closed systems which interaction with the environment is restricted to heat exchange and work, such a generalization of thermodynamics engendered numerous difficulties far from being publicly recognized. They were partly overcome by Gibbs with the mass M_k or the number of moles of the kth substances N_k used as additional state variables. However, some of the difficulties arisen have lasted out till the present and manifested themselves in especially the indeterminacy of the concepts of heat and work in open systems, unsuccessful attempts to solve the "Gibbs paradox", loss of potential properties by free energy, inapplicability of the law of the excluded perpetual motion of the second kind to open systems, etc. Some processes in open systems appeared to have been so peculiar that "to explain and confirm their behavior from the classic concepts does not look like possible" (M. Mamonov, 1970). Such are the diffusive processes with uncontrollable substance flow across the system borders, chemical processes of isothermal adiabatic fuel combustion in calorimeter, etc. There are, in particular, systems not allowing for even imaginary impenetrable membrane placed in their borders with the process being undisturbed (M. Tribus, 1970). In-depth investigation of such systems leads to a conclusion that "thermodynamics of variable-mass bodies…has regarding classic thermodynamics the same degree of the methodological self-sufficiency as thermodynamics of irreversible processes" (M. Mamontov, 1970).

Of more interest is, therefore, to investigate open systems from the positions of energodynamics enabling consideration of internal processes in isolated systems not recurring to the formalism above described.

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[1] The term "diffusion" (from the Latin "diffusio" meaning spreading) refers, strictly speaking, to the irreversible process of equalizing concentrations of some substances when distributing all over the system volume. This process features composition invariability of the system as a whole (unlike diffusion of the kth substances across the system borders). Therefore hereafter we will distinguish the diffusion in a strict meaning of this word from the selective.

10.1. Discrimination between Ordered and Unordered Works

Wishing to generalize the joint equation of the first and second laws of classic thermodynamics in the form of Gibbs' relationship (6.1.1) to systems doing other kinds of work beside expansion work the authors of many guidelines in thermodynamics express this equation as:

$$dU = \Sigma_i \Psi_i \, d\Theta_i, \quad (i = 1,2,\ldots,n) \tag{10.1.1}$$

where U – internal energy of the system; Ψ_i, Θ_i – values named the "generalized forces" and "generalized coordinates".

Such an "extension" of the law of conservation of energy in the form of (2.2.7) using the concepts of generalized force and generalized coordinate introduced yet by Lagrange seems to many investigators so natural that it is often applied without whatever substantiation. In particular, equation (10.1.1) is often applied to the analysis of surface phenomena representing work as (V. Sychev, 1986):

$$đW_f = \sigma_f df, \tag{10.1.2}$$

where Ψ_i is construed as the surface tension σ_f, while the coordinate Θ_i – as the body surface f. Meantime, a multiphase system is spatially heterogeneous and internally non-equilibrium, which is evidenced by existing pressure gradient on the phase boundary:

$$đW_f = (p' - p'')dV', \tag{10.1.3}$$

where p', p'' – gas pressure in the cohabiting phases (e.g. steam and liquid). Hence, this expression reflects processes in spatially heterogeneous media and refers to the terms of the second sum (2.2.5).

The same often the generalized forces appear to include in their number the intensities of electric **E**, magnetic **H** and other external fields, while the generalized coordinates Θ_i – the vectors of polarization **P** and magnetization **M.** However, dielectrics and magnetics are internally non-equilibrium systems – the fact which may be easily confirmed if observing the vector relaxation processes after their isolation from the external force fields. Their spatial heterogeneity is manifested in the opposite sign the unlike charges or poles displace when electric and magnetic dipoles are generating.

Expression (10.1.1) is often applied to the complex strain processes by substituting the pressure P for the pressure tensor **P**, while the volume V – for the strain tensor **T**. But for all that it is omitted that this tensor contains the components characterizing the deviation of the system from equilibrium, i.e. describing processes in non-equilibrium systems. This may be simply instantiated by the uniform extension of a rod, which strain work is usually expressed as:

$$đW_\ell = F_\ell \, d\ell \; . \qquad (10.1.4)$$

The value Ψ_i is herein construed as the extension force modulus F_ℓ, while Θ_i – as the rod length ℓ. Meantime, a stressed rod is as well non-equilibrium system where the state of different parts varies opposite (the displacements $d\ell$ of different halves of the rod in its center-of-mass system have opposite signs: $d\ell' \leq 0$, $d\ell'' \geq 0$). Therefore the work to extend the rod actually refers to the terms of the second sum in (2.2.5), which have vector nature:

$$đW_\ell = \mathbf{F}_\ell' \cdot d\mathbf{\ell}'/2 + \mathbf{F}_\ell'' \cdot d\mathbf{\ell}''/2 = \mathbf{F}_\ell \cdot d\mathbf{\ell} \; . \qquad (10.1.5)$$

It comes down even so far that equation (10.1.1) is applied to systems within the gravity field, where Ψ_i is construed as the gravity field intensity **g**, while Θ_i – as the distance between the body and the "field source" $\mathbf{r}_g$. However, the work to displace a body within the gravity field does not influence its internal state and may not enter the internal energy balance equation (R. Haase, 1967; I. Bazarov, 1991).

Therefore the transfer of the laws of thermodynamics to mechanical and electromechanical phenomena involving the external energy of systems under investigation should be done with great caution. The coordinates $\mathbf{r}_i$ of centers of mass, inertia, gravity of a system and of whatever energy carrier Θ_i refer to the external parameters of the system (I. Bazarov, 1991) and, hence, characterize the external energy of the system. Therefore a formal in-one-group integration of processes relating to principally different categories involving separately the internal and external energies of the system and described by the two different sums of equation (2.2.5) can not be construes otherwise than just an "adaptation to classic". This has a lot of negative consequences.

First of all, including "other kinds of work" most often means a tacit change to consideration of spatially heterogeneous media. Such media according to (2.2.6) have a double, while in a more general case of (2.2.5), even a triple number of degrees of freedom. This means that each new form of energy of the system, to be described, demands three additional parameters of Θ_i, r_i and φ_i types to be generally introduced. How-

ever, only one independent coordinate Θ_i in (6.1.1) corresponds to any additional degree of freedom. This generally leads to an "under-determinacy" of the system with all methodological and mathematical errors ensuing.

The main feature of this kind of work is that it is associated with transfer of the ith kind energy U_i by its energy carrier Θ_i from the environment into the system (or visa versa). Denoting, according to (2.6.1), this part of the coordinates Θ_i variation in the system and environment in terms of $d_e\Theta_i'$ and $d_e\Theta_i''$, respectively, while the potentials Ψ_i – in terms of Ψ_i' и Ψ_i'', respectively, the elementary work $đW_i^{dis}$ may be herein expressed as:

$$đW_i' = \Psi_i'd_e\Theta_i' \; ; \; đW_i'' = \Psi_i''d_e\Theta_i''. \qquad (10.1.6)$$

Since $d_e\Theta_i'' = - d_e\Theta_i'$, then at $\Psi_i' = \Psi_i''$ works $đW_i'$ and $đW_i''$ are numerically equal. This means that in the reversible process of disordered work the energy transfer across the system borders occurs without energy form variation. Therefore the work of such kind may be defined as a *quantitative measure of energy transfer process*. In particular, bodies, at the reversible heat transfer, exchange internal heat energy, while at the reversible expansion –strain energy, at the electrization – electrostatic energy, etc.

Hereto should also be referred the "gas introduction work" $W_{in} = \int\psi_\upsilon dM$, where $\psi_\upsilon = pv_k$ – the so called "hydrodynamic" potential; the work of charge Θ_e introduction into a zone with the φ potential (named here for short the electrization work) $W^{in} = \int\varphi d\Theta_e$; the so-called "chemical work" $W_k^d = \int\zeta_k dM_k$ characterizing the energy exchange at diffusion of the kth substance into the system; the work due to varying kinetic energy of reciprocal (diffusive) motion of mixture components $W_k^{dif} = \Sigma_k\int w_k dP_{k\alpha}$ (where w_k, $P_{k\alpha}$ ($\alpha = 1,2,3$) – velocity and momentum component of the kth substance in its motion relative to the center of mass); the work of momentum turbulent transfer inside the system $W_{\omega\alpha}^T = \int\omega_{k\alpha}d(\zeta_k \omega_{k\alpha})$, where $\omega_{k\alpha}$, $M_k\omega_{k\alpha}$ – components of, respectively, angular velocity and angular momentum of the kth system component. The heat exchange $Q = \int TdS$ should also be referred to this category if construed as a "micro-work" done on gas- or liquid-borne particles at their spontaneous motion acceleration. All these kinds of work vary only the system internal energy and are not associated with overcoming the resultant $\mathbf{F}_i$ of whatever forces. Therefore in thermokinetics demanding maximal generality we refer to these kinds of work as non-technical work, while in a more general case of non-technical disciplines – *anordered work* (failing a more adequate term) and denote them as W_i^a.

Another kind is the ordered work which consideration demands the force $\mathbf{F}_{ik}$ to be introduced in thermodynamics though primordially alien to it. Such a work is done on only spatially heterogeneous systems when some force couple $\mathbf{F}_{ik}$ is applied to subsystems with opposite sign of the Θ_{ik} property, e.g., to positive and negative charges, north and south poles of magnetic dipoles, electrons and holes in metals, areas with the parameter Θ_i density higher and lower as compared with the mean value, etc. The state variations caused by such kind of processes correspond to the principle of their opposite directivity (Chapter 1). Coordinates of such kind of processes (i.e. the parameters that necessarily vary with the processes running) are understood, as shown in Chapter 2, as the "displacement vectors" $\Delta\mathbf{r}_i$ or "distribution moments" $\mathbf{Z}_i = \Theta_i\Delta r_i$ associated with the resultant forces $\mathbf{F}_i$ or their specific values $\mathbf{x}_i = \mathbf{F}_i/\Theta_i = -\nabla\psi_i$ (thermodynamic forces), respectively. For a stationary process, where $(d\mathbf{r}_i\cdot\nabla)\psi_i = d\psi_i$, the analytic expression of the useful work W_i^e, according to (2.2.9), may be simplified to:

$$W_i^e = \int \mathbf{X}_i\cdot d\mathbf{Z}_i = -\int \Theta_i d\psi_i = -\Theta_i(\psi_i'' - \psi_i'), \qquad (10.1.7)$$

where ψ_i', ψ_i'' – generalized potential value at the energy carrier Θ_i inlet and outlet to/from the system, respectively.

As seen, useful work is associated with the variation of the particular kind of energy $U_i = \Theta_i\psi_i$ when the energy carrier crosses the system borders, i.e. when the energy transmutes from some of its form into another. Therefore useful work is a *quantitative measure of the energy conversion process*. The vector character of the variables describing this work category is its distinctive feature.

Along with these categories of work one more category exists featuring a conversion of energy from ordered form into disordered one. Such work is usually named dissipative W_i^{dis}. It features the initial form of energy having its resultant $\mathbf{F}_i$, however, in course of energy conversion the dissipative forces have to be overcome, which do not have a resultant. Therefore in course of the dissipative work ordered forms of energy are converted into disordered ones (including heat). Thus the dissipative work may be expressed thru parameters of both initial (ordered) and final (disordered) forms of energy. This directly ensues from the equations of balance for these works (2.4.5) and (2.4.6), according to which:

$$đW^{dis} = -\Sigma_i\int\mathbf{j}_i^p\cdot\nabla\psi_i dV = \Sigma_i\int\psi_i\sigma_i\, dV, \qquad (10.1.8)$$

where $\mathbf{j}_i^r$ – relaxation component of the ith energy carrier flow Θ_i; σ_i – density of the internal sources for this value.

In particular, in terms of system parameters the dissipative work may be expressed caused by dying-out of relative motion of components at their diffusive mixing (not influencing the momentum of the system in whole) $W_k^{dif} = \Sigma_k \int w_k dP_k$, the material destruction work $W_d^{dis} = \int \sigma_f df$ associated with the material surface f increase (where σ_f – surface tension) at breaking of solid and liquid materials, metal cutting, etc. Thus the energy dissipation generally consists not only in the conversion of ordered forms of energy into heat, but also into any other disordered kind of energy. Mathematically this is expressed in the "scalarization" of the energy components in a system, i.e. in the conversion of its inergy $E(\mathbf{Z}_i)$ into the anergy $\bar{U}(\Theta_i)$.

The vector variables $\mathbf{F}_i$ and $\mathbf{r}_i$ being absent in the generalized equation for the 1st and 2nd laws of classic thermodynamics, has led to failure to understand the distinction in kind between the first and second sums in (2.2.5). That is why, as shown above, the vector processes have been attributed just to a category of "other kinds of work" a polyvariant system does besides the expansion work. A more grave methodological error, as will be shown hereafter, lies in the conclusion about the energy "total convertibility" in the process of doing any kind of work (J. Szargut, R. Petela, 1968; I. Bazarov, 1976, et al.).

One more of the methodological errors lies in the deep-rooted belief that homogeneous systems can do useful work, too. Such a conclusion is based on the fact that, e.g., in homogeneous isobaric-isothermal chemical reactions such a work can be found from the Gibbs' energy decrease $G = U + pV - TS$. However, the circumstance is here disregarded that useful work in chemical reactions can be done only with chemical potential gradients or differences available, which demands a spatial separation of the reagents. It is precisely what is realized in such devices as the Vant-Hoff's equilibrium box, the voltaic or fuel cells. In the absence of such a separation chemical reactions inevitably become irreversible and releasing only dissipation heat numerically equal to the above Gibbs' energy decrease.

Thus, only the notion of force being introduced, the comprehension comes that "there is a difference between the two works".

10.2. Solution to the Problem of Thermodynamic Inequalities

The real processes running with a finite rate are known to represent a sequence of non-equilibrium states. The relaxation processes inevitable in this case force spontaneous variations of the entropy S, volume V and some other state parameters. This fact is reflected in the equations of their

balance like (2.4.1) and (3.3.4). As a result, the classic equations of the process elementary heat đQ and expansion work đW go over into the inequalities:

$$\text{đ}Q \neq TdS \; ; \; \text{đ}W_p \neq pdV, \tag{10.2.1}$$

and the so-called problem of thermodynamic inequalities arises not solved yet.

The intensity of processes increases, inequalities (10.2.1) aggravate, and the calculation of the system external energy exchange, based on them, becomes increasingly non-rigorous. For all of that classic thermodynamics itself is incapable to estimate the error associated with disregard of the said inequalities since their exact analytical expressions remains unknown.

This problem is accentuated for open and polyvariant systems doing, besides the expansion work, other kinds of work W_j (e.g. the work of introducing the kth substances into the system, work against surface tension forces, polarization and magnetization). In this case not only the masses M_k of the kth substances as system components can arbitrarily vary (due to internal chemical transformations), but also the coordinates $\mathbf{Z}_i$ of all kinds of useful work (due to system relaxation). This fact is reflected in balance equations (2.4.1) and (2.4.2) and results in the inequalities for also the energy-mass exchange đU$_k$ and all kinds of the useful work đW_i^e:

$$\text{đ}U_k \neq \mu_k dN_k; \; \text{đ}W_i^e \neq \mathbf{X}_i \cdot d\mathbf{Z}_i . \tag{10.2.2}$$

The reason for which the thermodynamic inequalities appear becomes evident enough if considering the issue from the positions of thermokinetics. With this purpose let us consider the equation of balance of various coordinate "wells" in the form of (2.4.7) or (2.4.8). This balance is provided due to compensation of the "wells" $d_u\Theta_i$ of the certain coordinates (the entropy, the kth substance masses, the volume, etc.) by the "sinks" $d_u R_j$ of others (i.e. by equalization of distributing the parameters Θ_i all over the system). However, the basic identity of thermokinetics in the form of (2.4.7) immediately goes over into an inequality along with balance equation (2.4.8) if excluding some of its actual terms allowing for the sinks $d_u\mathbf{R}_j$. This is what happens to the equations of classic thermodynamics because of the absence therein the non-equilibrium state parameters $\mathbf{X}_i$ and $\mathbf{Z}_i$. Thus the inequalities are caused by the said underdeterminacy of a system, i.e. by an attempt to take irreversibility into account not allowing explicitly (with the help of the non-equilibrium parameters and their sinks) for its reason – the spatial heterogeneity. In fact, there are no reasons in spatially homogeneous and chemically neutral

media, which would cause a spontaneous variation of whatever thermostatic variables Θ_i, i.e. their wells or sinks appearing. Should these wells or sinks nevertheless appear, this means some uncounted reasons exist.

Equation (2.3.7) suggests the way out when implying the possibility to represent the external energy exchange directly in terms of the energy carrier flow $\mathbf{j}_i^e$ across the system borders. Indeed, the variation $d_e\Theta_i$ of any coordinate Θ_i due to its transfer across the borders of a stationary system can be represented in terms of its local flow $\mathbf{j}_i$ density:

$$d_e\Theta_i/dt = -\int \nabla\cdot\mathbf{j}_i^e \, dV . \qquad (10.2.3)$$

From this it follows that the terms of the first summand (2.3.7) give the exact analytical expression for the work of unordered character (process capacity $N_i^{un} = đW_i^{un}/dt$), where ψ_i is a local value of the generalized potential on the system border:

$$N_i^{un} = \int \psi_i \nabla\cdot\mathbf{j}_i^e \, dV = \int \psi_i \mathbf{j}_i^e \, df. \qquad (10.2.4)$$

The flows $\mathbf{j}_i^e$ can be measured with heat meters, ammeters, flow meters, and other devices, while the potentials ψ_i – with temperature sensors, pressure sensors, etc. This enables in principle to solve the problem consisting in direct definition of the system energy exchange in a variety of conditions and to retain, at the same time, the phenomenological character of the classic theory for nonequilibrium thermodynamics.

In spatially homogeneous (internally equilibrium) systems the potentials ψ_i are the same for all points of the system and can be factored outside the integral sign. This corresponds to the infinitely slow (quasistatic) state variations, i.e. to the so-called reversible processes. Then $\int \nabla\cdot\mathbf{j}_i^e dV = d\Theta_i/dt$ and relation (10.2.4) is simplified going over into (2.3.2). Table 10.1 illustrates the exact analytical expressions for heat exchange, mass exchange, expansion work and other unordered works in reversible and irreversible processes as based on (10.2.4). All kinds of unordered works (including heat exchange and mass exchange) are assumed in the table as positive if augmenting the system energy.

Most of the expressions for reversible energy exchange shown in the table are known from classic thermodynamics with the exception of probably the energy-mass exchange at diffusion of the kth substance wherein the chemical potential μ_k gives place to the diffusive ζ_k and osmotic ς_k potentials in line with the corrected notions of heat in open systems (see Chapter 5). Of interest are also the expressions for accretion work – an increment in the mass of a star with a substance dropped onto its surface from outside, which is the gravitational analog of the gas-enter work.

Table 10.1

Exact Analytical Expressions for Unordered Works

Process	In reversible proc., dW_i^{un}, J	In irreversible proc., N_i^{un}, W	Note
Substance Enter	$dW_{in} = p\upsilon dM$	$-\int p\upsilon \mathbf{j}_m^{\mathrm{e}} \cdot d\mathbf{f}$	$\mathbf{j}_m^{\mathrm{e}}$ – substance flow f across surface
Cubic Strain	$dW_p = -pdV$	$\int p \mathbf{j}_\upsilon^{\mathrm{e}} \cdot d\mathbf{f}$	$\mathbf{j}_\upsilon^{\mathrm{e}}$ – surface f displacement velocity
Chemical Reaction	$dW_{\mathrm{x}} = A_r d\xi_r$	$-\Sigma_k\int \mu_k \mathbf{j}_k^{\mathrm{e}} \cdot d\mathbf{f}$	μ_k – chemical potential
Diffusion of the kth Substance	$dU_k = \zeta_k^{\mathrm{D}} dN_k$ $(p,T=\mathrm{const})$	$-\int \zeta_k \mathbf{j}_k^{\mathrm{e}} \cdot d\mathbf{f}$	$\mathbf{j}_k^{\mathrm{e}}$ – k^{th} substance flow
Heat Exchange	$dQ = TdS$	$-\int T \mathbf{j}_s^{\mathrm{e}} \cdot d\mathbf{f}$	$\mathbf{j}_s^{\mathrm{e}}$ – entropy flow
Osmosis of the kth Substance	$dU_k = \varsigma_k^{\mathrm{os}} dN_k$ $(V,T=\mathrm{const})$	$-\int \varsigma_k \mathbf{j}_k^{\mathrm{e}} \cdot d\mathbf{f}$	$\mathbf{j}_k^{\mathrm{e}}$ – solvent flow
Electrization	$dW_e = \varphi d\Theta_e$	$-\int \varphi \mathbf{j}_e^{\mathrm{e}} \cdot d\mathbf{f}$	$\mathbf{j}_e^{\mathrm{e}}$ – electric current
Star Matter Accretion	$dW_{ac} = \psi_g dM$	$-\int \psi_g \mathbf{j}_m^{\mathrm{e}} \cdot d\mathbf{f}$	ψ_g – gravitational potential

The table is primarily attractive with the generality of the analytical expressions for all kinds of unordered works. This emphasizes the fact that, as a result of this category of processes, a system remains internally equilibrium, i.e. acquires inconvertible energy (anergy) and, therefore, remains incapable for work. This is the reason why, in order to convert the energy obtained from such energy exchange processes, a system is required not being in equilibrium with this energy and, therefore, capable to play the part similar to the heat sink in classic thermodynamics.

The basic equation of thermokinetics (2.3.7) gives also exact analytical expressions for the useful (ordered) external works W_i^{e}. The analytical equations derived from the above expression are for convenience tabulated in Table 10.2.

As follows from the table, the possibility to find exact analytical expressions for ordered and unordered works is based on their representation in terms of the measurable energy carrier flow $\mathbf{j}_i^{\mathrm{e}}$ across the system borders [1].

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[1] In heat engines the energy carrier transit flow J_i^{e} sometimes changes with additional entropy flows added to it. This phenomenon is taken into account with the help of the "reheat factor". In such cases the flow J_i^{e} can not be factored outside the integral (6.5.6) sign. Nonetheless, the expression (6.5.6) is here more practical for use.

Table 10.2

Exact Analytical Expressions for Ordered Works

Process	In reversible processes $đW^e$, J	In irreversible processes N_i^e, W	Note
Heat Transformation	$-SdT$	$N_q = -\int J_s^e\, dT$	J_s^e – entropy flow
Gas Work in Flow	$-Vdp$	$N_p = -\int J_\upsilon^e\, dp$	J_υ^e – flow rate
Liquid Injection	$-Mdh$	$N_m = -\int J_m^e\, dh$	J_m^e – liquid flow rate
Chemical Reaction	MA_r	$N_x = -\int J_r^e\, d(A_r\xi_r)$	J_r^e – reagents flow rate, A_r – affinity
Binary Mixture Separation	$-N_k d\psi_k$	$N_\text{д} = -\int J_k^e\, d\psi_k$	$\psi_k - k^{th}$ potential
Electric Charge Displacement	$-\Theta_e d\varphi$	$N_e = -\int J_e^e\, d\varphi$	J_e^e – circuit current, φ – electric potential
Dielectric Polarization	$-\mathbf{E}\cdot d\mathbf{P}$	$N_\text{п} = -\int J_e^c\, d\varphi$	J_e^c – displacement current
Body Acceleration	$-\mathbf{P}\cdot d\mathbf{v}$	$N_k = -\int J_w^e\, dv$ v – скорость	J_w^e – momentum flux
Displacement in Gravitational Field	$-Md\psi_g$	$N_g = -\int J_m^e\, d\psi_g$	ψ_g – gravit. potential

In accordance with the flow balance equations (2.4.3) this equation distinguishes that part of the redistribution processes which is not associated with the relaxation processes (the relaxation flows $\mathbf{j}_i^r$). Such a way of the energy exchange definition is valid irrespective of the fact whether the consequent processes in the system itself are reversible or irreversible. This gives the most acceptable (to date) solution to the problem of thermodynamic inequalities.

Comparison between Tables 10.1 and 10.2 shows also that the true "dividing ridge" in real processes lies not in-between heat and work (as it has always been in equilibrium thermodynamics), but rather in-between two qualitatively different categories of effects referred here as to ordered and unordered works.

10.3. Generalisation of Second Law on Non-Heat Engines

It is often confirmed as going without saying that the maximal efficiency η_i of any non-heat engine consuming the energy from a well in the form of work is always equal to unity:

$$\eta_j = W_j/U_i' = 1. \qquad\qquad (10.3.1)$$

Here W_j – work done by a non-heat engine; U_i' – energy supplied to a system by doing work on it. Such an assertion of the "exclusiveness" pertaining to heat engines is based on the belief that heat and work are in principle unequal because the latter can "directly apply to augment any form of system energy, whereas heat – to replenish the internal energy only" (I.P. Bazarov, 1991). The "substantiation" of this assertion usually appeals to such kinds of work as bar extension, charge displacement in electric field, load lifting, body acceleration, polarization, magnetization, etc, i.e. to useful (ordered) kinds of work. However, the fact is missed in this case that the useful external work is done on a spatially heterogeneous (expanded) system as a whole and replenishes the ordered part of its internal energy (inergy) measured by the amount of this work exactly. As shown above, the useful external (ordered) work as itself is a quantitative measure of the energy conversion process. Therefore raising the question about the convertibility rate of the energy as applied to a heterogeneous system through doing useful work on it is the tautology as itself. It is quite another matter if concerns the convertibility rate of the energy as applied through doing unordered kinds of work, to which, in accordance with the above, the "microwork" at heat exchange should be attributed. This is exactly the case revealing that the "idea about impossibility of the perpetual motion of the 2nd kind if shrunk to the statement about the exclusive properties of heat wells is unjustified from the methodological standpoint" (A. Gukhman, 1947).

To make sure that the extrapolation of the energy conversion laws to unordered kinds of work is inadmissible with the energy supplied to a system in the form of ordered work, let us consider some working medium capable for expansion, heat exchange and exchange of the kth substances, electrical charge, etc with the environment. If such a body (subsystem) is spatially homogeneous, the replenishment of its unordered energy (anergy) as a result of an unordered work W_i done on it is expressed, according to (2.2.5), as:

$$dU_i = \Psi_i\, d\Theta_i \, . \, (i = 1, 2, \ldots, n) \qquad\qquad (10.3.2)$$

where Ψ_i – generalized force (absolute pressure p, chemical, electrical, etc potentials of the system); Θ_i – generalized coordinates (system volume with the opposite sign $-V$, number of moles N_k of the kth substance, bulk electrical charge Θ_e, etc).

To avoid the expenditure of a working medium during the conversion of the energy U_i received from a well, let us compel the medium to run a cyclic process. The work of such a cycle is

$$W_\text{ц} = \oint \psi_i d\Theta_i \qquad (10.3.3)$$

It follows from this expression that the useful work $W_j = W_c$ of the cyclic machine under consideration is different from zero in only the case when the potential ψ_i takes different values for different parts of the cycle. Otherwise, factoring ψ_i outside the integral sign (10.3.3) and considering that the circuital integral of any state parameter $\oint d\Theta_i = 0$ gives $W_j = 0$. Thus in any cyclic machine the working medium must contact at least two wells of the convertible energy U_i with different potential values ψ_i' and ψ_i'' (analogs of the heat well and heat sink in the theory of heat engines). Then dividing the circuital integral on the right-hand side of (10.3.3) into two parts where $dU_i' = \psi_i' d\Theta_i > 0$ (energy is supplied to the working medium)) and $dU_i'' = \psi_i'' d\Theta_i'' < 0$ (energy is withdrawn from it), respectively, and denoting the mean values of the potentials for these parts as $\overline{\psi}_i'$ and $\overline{\psi}_i''$ (Fig. 3.1) with consideration that $d\Theta_i'' = -d\Theta_i'$ gives :

$$đW_j = (\overline{\psi}_i' - \overline{\psi}_i'')d\Theta_i' \text{ или } W_j = (\overline{\psi}_i' - \overline{\psi}_i'')\Theta_i^{*} . \qquad (10.3.4)$$

where $\Theta_i^{*} = \int d\Theta_i''$ – amount of energy carrier from its well to its sink.

From this it follows that the absolute efficiency η_j of a cyclic engine converting the arbitrary i^th form of the homogeneous system energy may be expressed in much the same way as the heat engine thermal efficiency (4.2.3):

$$\eta_j = W_j/U_i' = 1 - \overline{\psi}_i'' / \overline{\psi}_i' . \qquad (10.3.5)$$

From this expression it can be seen that the efficiency for a cyclic converter of unordered energy in any form is defined by exclusively the relation between the mean integral values of the potential corresponding to supply and withdrawal of the energy being converted and is always below unity since the values $\overline{\psi}_i'' = 0$ or $\overline{\psi}_i' = \infty$ are physically unrealizable.

By way of example let us consider a cyclic-action electrostatic engine converting external electrostatic energy of some charged body. The engine is a plane capacitor with sliding plates. In such a device the electrostatic energy U_e' is supplied by entering the electric charge Θ_e with the elementary work $dU_e' = \varphi' d\Theta_e$ done in this case to enter the charge $d\Theta_e$ into the area with the potential φ', while the energy is withdrawn by doing the work $dU_e'' = \varphi'' d\Theta_e$ to bring this charge out. The useful work is

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done here through transfer of the elementary charge $d\Theta_e$ from a charge well with the potential φ' to a charge sink with the potential φ'' and is equal to $dW_e = d(U_e' - U_e'') = (\varphi' - \varphi'')d\Theta_e$, which in relation to the well energy loss dU_e' gives the part

$$\eta_j = 1 - \varphi''/\varphi', \tag{10.3.6}$$

corresponding to relation (6.7.5). It is significant that the efficiency of such an electrostatic energy converter η_j for the quite real case of $\varphi' = 10^8\,V$ and $\Delta\varphi = 10^3\,V$ will amount at the most to one thousandth of a percent irrespective of the electrostatic generator design. Thus we stand very far from the possibility to use the "entire electric energy".

Let us consider now an "expansion" machine doing work through the pressure difference between the working medium p' and the environment p''. The work done in this case will be defined as $dW_p^e = (p' - p'')dV$, while the well energy loss will amount to $dU = p'dV$ according to (6.7.2). Hence the work done in this case makes up only a part of the well energy loss and is determined as (10.3.5). This part is defined by the environmental pressure which is known to be different from zero.

The same result can be obtained from consideration of non-cyclic open-type engines where the working medium is the substance of the energy well itself, while the sink is the environment wherein the working medium enters after the work done. In such machines the energy dU' is supplied by entering the kth substance in the amount of dN_k moles with the molar enthalpy h_k', while the energy dU'' is withdrawn by bringing this substance out with the enthalpy h_k''. Then $dU' = h_k'dN_k$, $dU'' = h_k''dN_k$ and the work done $dW_k = d(U' - U'') = (h_k' - h_k'')dN_k$. Thus the efficiency of the open-type engines (e.g. magneto-hydrodynamic energy generators operating in open circuit) is characterized through the so-called "enthalpy" efficiency (Favorsky, 1978):

$$\eta_i = 1 - h''/h', \tag{10.3.7}$$

where h', h'' – enthalpy of the working medium at the generator inlet and outlet, respectively. Since the enthalpy of dissociated and ionized gas is by no means proportional to its temperature, this efficiency will essentially differ from the thermal efficiency at the same temperatures of working medium.

The said directly concerns the engines using the external kinetic and potential energy. The "adaptation to the classics" for such systems as force fields or velocity fields usually means that the intensities of these fields (expressed in terms of the potential gradients $\nabla\psi_i$) are taken for the "generalized forces" Ψ_i, while the value of the energy carrier $\Theta_i^* = \Delta\Theta_i''$

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transferred from some field point to another – for the "generalized coordinates" Θ_i themselves. Meanwhile, equilibrium thermodynamics if correctly applied to them requires due consideration of the fact that these fields are formed by heterogeneously distributed material bodies with the masses M_1, M_2, …, M_n or the charges Θ_1, Θ_2, …, Θ_n, which change their state in opposite way: some of them receive a charge or a mass, whereas others lose them, on the contrary. Thus, to set the problem in the same form as for heat engines, some of these subsystems should be considered as energy wells, whereas others – as energy sinks. By way of example let us consider an engine that uses the gravitational energy U_g. A body with a mass of M_1 introduced into this field has the gravitational potential $\Psi_g = U_g/M_1 = -GM_2/R = U_g/M_1$, where M_1, M_2 – masses of the field-forming bodies, G – gravitation constant, R – center-to-center distance of the gravitating masses.

Let now one of the bodies with a mass of M_1 give the part dM_1 of its mass to the working medium passing from a field point with the gravitational potential ψ_g' to a point with the potential ψ_g'' doing at that the work $dW_g = (\psi_g' - \psi_g'')dM_1$. This value is less than the energy $dU_g' = \psi_g' dM_1$ the working medium receives in this case so that the relation between them exactly corresponds to expression (10.3.5). Note that the absolute efficiency of such a "gravitational" engine is below unity since the value $\psi_g'' = 0$ corresponds to the infinite distance in-between the interacting bodies and is, hence, unrealizable. Note furthermore that the same conclusion can be obtained as a short cut through relation (10.3.7).

Thus the laws of energy conversion in any unordered form appear to be unitary and in classic thermodynamics if, in accordance with its methodology, the object of investigation is construed as a homogeneous system all parts of which similarly change their state in processes under investigation. In this case a necessity arises in another body available not being in equilibrium with the energy well and capable to play the part of the energy sink, i.e. a necessity in the availability of a nonequilibrium system. Such a nonequilibrium system classic thermodynamics considers may be instantiated as the so-called "expanded" systems comprising the environment as energy sink. This statement is reasonable to be called for easy reference as the **energy convertibility principle**: *everywhere relaxation processes are running the useful conversion of energy is also possible.*

In this case even at $\varphi'' = 0$ there is direct evidence of the second criterion of the "compensation" for energy conversion process R. Clausius mentioned – the transfer of some part of energy carrier (which quantitative measure is the parameter Θ_i) from energy well to energy sink with changing the state of not only the well, but also other subsystems involved in the process (in opposite way though). Note the question here is

not the inevitable losses, but rather the principal unattainability of 100% conversion of the energy obtained through the $\psi_i d\Theta_i$ impact, i.e. by the *energy transfer* (unordered work done). The other challenge issued as the conversion of the energy supplied to a system through such an action as the useful work $\mathbf{X}_i \cdot d\mathbf{Z}_i$ ($\mathbf{E} \cdot d\mathbf{P}$, $\mathbf{H} \cdot d\mathbf{B}$, etc) is a departure from the classic problem definition.

Meanwhile, this is exactly the way investigators choose when construe the parameter Ψ_i as the voltage $\Delta\varphi = \varphi' - \varphi''$ across the capacitor plates or the fuel cell electrodes and the coordinate Θ_e – as the charge $\Delta\Theta_e$ transferred in-between them (which is, by the way, the function of process rather than state). In this case, naturally, the "deduction" is inevitable of complete convertibility of electric or other energy. This does not come as a surprise since in this case the electric energy $dU_e' = \Psi_i d\Theta_i$ supplied to the converter appears to be identical with the useful work $\bar{d}W_e = (\varphi' - \varphi'')d\Theta_e$ it does. However, it is easy to show that such a conclusion means the violation of the equilibrium thermodynamics applicability conditions. Indeed, any extensive parameter in equilibrium thermodynamics characterizes the state of an entire system and varies uniformly in all its parts. This statement is evidently violated in the abovementioned nonequilibrium systems, different parts of which (subsystems) change their state oppositely in the course of energy conversion. Such subsystems may include not only the heat wells and heat sinks in the classic theory of heat engines (which oppositely change their entropy), but also the opposite charges moving in the opposite directions or opposite poles of polarized and magnetized bodies, the electrons and holes in semiconductors, the opposite plates of capacitors, the positive and negative ions in electrolytes and plasma, the spin systems and atomic lattice in crystals. It is easy to make sure that all these systems are nonequilibrium when observing the arbitrary variation of their state after having been isolated from the environment. The consideration of such systems, strictly speaking, outsteps the applicability of classic thermodynamics since their behavior conflicts with the fundamental "equilibrium self-non-disturbance principle" (general law) of classic thermodynamics. According to this principle the state of a thermodynamic system can be changed by only an impact from outside. Since this condition is evidently violated in nonequilibrium systems, the latter, from the position of classic thermodynamics, should be divided into spatially homogeneous areas, phases or components, to which the equations of equilibrium thermodynamics are solely applicable. This is the violation of this condition that underlies the erroneous division of various energy forms into "completely convertible" and "incompletely convertible" (A. Dolinsky, V. Brodyansky, 1991). Any form of energy is convertible inasmuch as it is internally nonequilib-

rium and the relation between its ordered and unordered parts is a measure of this nonequilibrium state.

It is possible to prove that the principle of excluded perpetual motion of the 2nd kind has the universal character for also continuums where wells and sinks of whatever kind of energy can be hardly distinguished. To do so, it is just necessary to use the body of mathematics for thermokinetics operating the notions of forces and flows. Indeed, as follows from relations (10.3.4), to do useful work, it is necessary here also to arrange a transfer of the energy carrier Θ_i from a subsystem with the potential ψ_i' to another one with the potential ψ_i''. This means that some areas of the continuum are wells, whereas others – sinks of the ith energy carrier. This is what means the "compensation", which necessity R. Clausius has stated. In this case the work W_i^e according to (10.3.4) makes up relative to the supplied energy $U_i' = \psi_i'\Theta_i$ the same part (10.3.5) as for heat engines. This fact evidences the unitary of the conversion processes for energy in any forms.

Some investigators recognizing the universality of expression (10.3.5) associate, nonetheless, the possibility to reach the 100% efficiency with the arbitrariness to choose the zero reference potential of energy carrier sink ($\psi_i'' = 0$) for non-heat forms of energy. Such arbitrariness really takes place in mechanics and electrodynamics operating external energy. For them the zero reference point is a matter of agreement. However, it is absolutely intolerable in thermodynamics, where the question as itself arose regarding the degree of heat convertibility into work. As a matter of fact, if it were not for the third law of thermodynamics (principle of unattainable absolute zero of temperature), then we, having the heat sink temperature taken for zero, would immediately come to the conclusion that the thermal efficiency could also be equal to unity. However, from the positions of thermodynamics the state of any bodies involved in processes under investigation or varying their state in whatever manner can not be taken as zero reference point for any of the system parameters. Otherwise, the system internal energy would vary also in the absence of energy exchange with bodies under consideration (only due to state variation of these reference bodies). That would violate the first law of thermodynamics which declares the internal energy existing as a state function and not depending on the position or movement of the system relative to those bodies. Hence the zero of whatever potential corresponds in thermodynamics to the "degeneracy" of movement (interaction) of a particular kind and to the loss of a particular degree of freedom by the system, which makes it inapplicable as energy sink.

Thus the conclusion of 100% efficiency for any non-heat engines is a consequence of a number of methodological errors, viz. departure

from the classic problem definition regarding heat engine, confusion of energy and anergy as notions, identification of technical and nontechnical (ordered and unordered) kinds of work, arbitrary choice of zero reference potentials.

It is worth noticing that along with the machines converting some i^{th} form of energy also such ones exist which use simultaneously several kinds of energy or several wells of the same form of energy. In all such cases the notion of efficiency also needs clarification since the work of such a machine is defined by the difference of several potentials Ψ_i. In such cases one can speak of only the conversion degree of the energy supplied from all its wells $\Sigma_j U_i'$, which corresponds to the efficiency expressed as:

$$\eta_i = W_i/\Sigma_j U_i' \ . \tag{10.3.8}$$

The universal character of the principle of excluded perpetual motion of the 2nd kind becomes much more understandable with the ban it declares removed and superseded by the condition necessary and sufficient to create heat engines. This condition finds its reflection in a famous dictum by S. Carnot, "*everywhere with a temperature difference available the thermal motive force is possible to appear*". In a more complex systems being in partial equilibrium the absence of some process or other may follow from the mutual compensation of thermodynamic forces $\mathbf{X}_j$ (i, j = 1, 2, …, n). This relates also to systems featuring heterogeneous temperature fields and being in gravitational, centrifugal, etc force fields. For such systems the deviation from internal equilibrium (the generalized potentials ψ_i unequal in some parts of the system) is already insufficient criterion for the absence of external equilibrium (ceased flow of energy of the ith kind between the system and the external field and its conversion into other forms of energy). That demanded to clarify the Carnot principle and to declare that external equilibrium with the force field to be necessarily absent. Such a generalization, by analogy with the Carnot principle, may be expressed as follows, "*everywhere with equilibrium being absent the useful conversion of energy is possible*". This statement is valid also for systems in external force fields.

10.4. Restoration of Potential Properties of Free Energy in Open Systems

The thermodynamic potentials, such as Helmholtz's $\Gamma = U - TS$ or Gibbs' $G = U - TS + pV$ free energy, are known to be inapplicable to open systems. To open the reasons of it, we will consider the incorpo-

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rated equation of 1st and 2nd beginnings of classical thermodynamics of open systems in the form of Gibbs' relationship (6.5.1), having replaced in it for convenience the mass of a kth substance their numbers of moles:

$$dU = TdS - pdV + \Sigma_k \mu_k dN_k, \qquad (10.4.1)$$

where μ_k – chemical potential of one asking k^{th} substances, J/mol.

Change of kth substance numbers of moles in open system can be called two reasons: diffusion of that substance through system borders (we will designate this part of dN_k according to the balance equations (2.5.1) through d_eN_k) and chemical reactions in system (designated as d_sN_k). We will use now a known ratio between number of moles any k^{th} substance in r^{th} chemical reaction dN_{kr} through its coordinate ξ_r, named by De Donde (1933) as degree of its completeness:

$$dN_k = \Sigma_k dN_{kr} = \Sigma_r \nu_{kr} d\xi_r, \qquad (10.4.2)$$

where ν_{kr} – Where ν_{kr} – stehiometric coefficient of in r^{th} chemical reaction.

Substituting (10.4.2) in (10.4.1) and applying to its other members the Legendre transformation $TdS = dTS - SdT$; $pdV = dpV - Vdp$, expression (10.4.1) can give a form

$$- dG = SdT - Vdp + \Sigma_r A_r d\xi_r + \Sigma_k \mu_k d_eN_k. \qquad (10.4.3)$$

Here the member $\Sigma_r A_r d\xi_r$ reflects the chemical reactions proceeding in considered open system under the influence of chemical affinity $A_r = $ = - $\Sigma_k \nu_{kr} \mu_k$ of kth substances and characterises the maximum work which such reaction can make. Last member (10.4.3) still characterises diffusion of kth substances through borders of open system. Thus, in open systems unlike (4.6.11)

$$- [dG]_{p,T} = \Sigma_r A_r d\xi_r + \Sigma_k \mu_k d_eN_k, \qquad (10.4.4)$$

i.e. the decrease of Gibbs' free energy in conditions p, T = const does not define any more the useful work $\Sigma_r A_r d\xi_r$ which chemically reacting system could make in case of reversible chemical reactions, and considers as well diffusion of kth substances through its borders as a version of mass exchange with environment. Thus, in classical thermodynamics of open systems really *there is no the potential which decrease would define the work made by system* (I. Bazarov, 1991; G. Gladyshev, 1988).

Consequences of loss by free energy of potential properties are extremely serious, as to such systems is not applicable also other thermodynamic method - a method of cycles, together with a principle of increase

of entropy which concerns also only the closed systems practically. Not surprisingly therefore an abundance in thermodynamics of open systems of paralogisms, completely not promoting understanding of their specificity.

Position becomes others if to use offered of energodynamics division of energy into the ordered and disorder parts (inergy and anergy). According to (2.3.5), inergy E of polyvariant and open system, i.e. its convertible part can be found «on return balance» as a difference between energy of system U and its equilibrium part $\bar{U} = \Sigma_i \Psi_i \Theta_i$ (anergy). To allocate this part, we will add to (10.4.1) and deduct from it member $\bar{\mu}_k \, dN_k$, in which $\bar{\mu}_k$ - chemical potential of kth substance in a condition of chemical balance of the same system. In that case

$$dU = TdS - pdV + \Sigma_k (\mu_k - \bar{\mu}_k) \, dN_k + \Sigma_k \bar{\mu}_k \, dN_k ,\qquad (10.4.5)$$

Here last member still characterises diffusion of substances through system borders, as for lack of chemical reactions $dN_k = d_e N_k$. On the contrary, the penultimate member addresses in zero only after end of all chemical reactions, when $\mu_k = \bar{\mu}_k$ и chemical affinity of system - $\Sigma_k \nu_{kr} \bar{\mu}_k$ = 0. As the substances N_k, added in the course of diffusion in system, are not changing differences $\mu_k - \bar{\mu}_k$, dN_k member $\Sigma_k (\mu_k - \bar{\mu}_k) \, dN_k$ is defined by the same expression (10.4.2). Therefore instead of (10.4.5) it is had:

$$dU = TdS - pdV - \Sigma_r A_r d\xi_r - \Sigma_k \bar{\mu}_k \, dN_k ,\qquad (10.4.6)$$

This expression can be spread out on two components, characterising change accordingly inergy and anergy of considered system:

$$d\bar{U} = TdS - pdV + \Sigma_k \bar{\mu}_k \, dN_k ,\qquad (10.4.7)$$

$$- dE_{ch} = - \Sigma_k (\mu_k - \bar{\mu}_k) \, dN_k = \Sigma_r A_r d\xi_r \qquad (10.4.8)$$

Thus, in open systems only part of Gibbs' free energy possesses of potential properties. This part is named here chemical inergy E_{ch}. Generally the decrease of inergy - dE defines the sum of all kinds of useful works $\Sigma_i \mathbf{X}_i \cdot d\mathbf{Z}_i$, made by system. All these kinds of works have the vector nature. With reference to chemical reactions it is expressed in the requirement of spatial division of reagents, for example, oxygen and the hydrogen submitted on electrodes of a fuel element. In case of homogeneous reactions their affinity is realised exclusively in the form of heat, i.e. reaction gets purely dissipative character. As process dissipation con-

sists in transformation of the ordered forms of energy in disorder, it is necessary to recognise, as homogeneous chemical reactions at microlevel represent the ordered process of change of a spatial configuration of molecules. Such systems we have named the microordered.

The similar approach to a finding of inergy can be applied and to other internal processes of system structure change, for example, processes of phase transformation in multiphase systems (V.Etkin, 1991). It is necessary to consider only, that from positions of energodynamics all coordinates are extensive sizes (as well as energy of system, which they define) and submitting to a uniform rule of signs ($d\Theta_i > 0$, $d\mathbf{R}_j > 0$ if $dE > 0$). Therefore it is expedient to enter in interests of unity instead of ξ_r size

$$|\mathbf{Z}_r| = N\nu_{kr}(1 - \xi_r),\qquad(10.4.9)$$

which pertinently to name *incompleteness* r^{th} reactions. Affinity of reaction A_r gets in this case according to (2.2.8) sense of thermodynamic force of rth chemical reaction X_r:

$$|\mathbf{X}_r| \equiv A_r = (\partial E/\partial Z_r).\qquad(10.4.10)$$

In case of phase transformation it is necessary to understand as its coordinate Z_λ the mass of kth substance M which have tested phase λ–transformation of 1st or 2nd sort as, and under ξ_λ and $\nu_{k\,\lambda}$ under ξ_λ and $\nu_{k\,\lambda}$ accordingly degree of phase transformation ($0 < \xi_\lambda < 1$) and concentration c_k this substance in the phase which has undergone λ–transformation ($\lambda = 1, 2, \ldots, \Lambda$). Then $dM_{k\lambda} = Mc_k\,d\xi_\lambda$, that corresponds to coordinate of this process $Z_\lambda = M(1 - \xi_\lambda)$ when for a positive direction of phase transformation what conducts to reduction of systems inergy and to heat allocation is accepted. This coordinate Z_λ pertinently to name *incompleteness* λ–*transition*.

Thus, in open chemically reacting systems the inergy possessts all properties of characteristic function, replacing of Gibbs energy. From here - that not passing role which will be played further this the most general measure of orderliness and working capacity opened and closed, simple and complex, macro-and microordered systems.

10.5. Correction of Material Equilibrium Conditions

Based on relationships (6.5.1) Gibbs was he first who defined the conditions of equilibrium distribution of the kth substances in heterogeneous systems. Those conditions consisted in equality of temperatures T, pressures p and chemical potentials μ_k of the kth substances in all parts of

such systems, which corresponded to heat, mechanical and material ("chemical" after Gibbs) equilibrium in them. Since the equilibrium in thermodynamics is construed as a state featuring a cessation of some macro-processes, it would be logic to assume that the above kinds of equilibrium mean the cessation of, respectively, heat transfer, cubic strain and mass transfer between the parts of a system under consideration. However, when that question was considered from the theory of irreversible processes (TIP), it became clear that the equality of chemical potentials μ_k was not yet a sufficient condition for the cessation of the kth substance redistribution (I. Prigogine, 1947; S. De Groot, 1956; R. Haase, 1967; etc.). It turned up that with the chemical potential gradients for all system components having become zero, i.e. with the Gibbs' material equilibrium conditions met, the kth substances redistribution did not cease, the transfer of those substances could occur also due to temperature gradient (thermo-diffusion, thermo-osmosis), pressure gradient (pressure diffusion, reverse osmosis), electric potentials (electro-osmosis, electrophoresis, electroplating), etc. However, the so-called "stationary states" were allegedly possible, when the flow of some k^{th} substance disappeared not because its motive force, viz. its chemical potential gradient, became zero, but due to other motive forces maintained in the system, which mitigated the process. On the other hand, according to TIP, when the redistribution of the kth substances is running, the thermal equilibrium can not be either reached since the heat-mass transfer (transfer of internal energy of kth substances' spontaneous motion) is possibly maintained in this case. A more than paradoxical situation has arisen, when the cessation of a process is no more the criterion of equilibrium reached, which violates the thermodynamic grounds themselves. Nevertheless, none of the investigators doubted the conformity of the J. Gibbs-found equilibrium conditions to the real circumstances. Meantime, that fact could have been noticed a long time ago due to the impossibility to define the chemical potential $\mu_k = (\partial U/\partial N_k)_{S,V,Nm}$ in such a way as expected from relationship (6.2.1), i.e. as a partial derivative at constant entropy S and volume V of the system. Actually, neither the volume $V = \Sigma_k N_k v_k$, nor the entropy $S = \Sigma_k N_k s_k$ particularly, being extensive values, do not remain, generally speaking, invariable with introducing the kth substance changing not only the composition (N_k/N), but also the mass (mole number) of the system (N). Unfortunately, instead of correction of the Gibbs' relationship the investigators preferred the stationary state theory having developed, where at the process cessation the phenomenological coefficients appeared as a function of the process rate and construed as neither thermodynamic variables, nor pure kinetic values (Chapter 4).

Meantime, the true form of the component potential is easy to be found. For this let us take into account that introducing the kth substance

should not vary the parameters s_{ko} and v_{ko}. Therefore considering the internal energy of the kth component U_k as a function of the independent variables s_{ko}, v_{ko}, N_k and noting that at N_k = const the derivatives $(\partial U_k/\partial S_{ko}) = T$ and $(\partial U_k/\partial V_{ko}) = -p$ (i.e. mean the same as in closed systems) gives:

$$dU = \Sigma_k N_k T ds_{ko} - \Sigma_k N_k p dv_{ko} + \Sigma_k \varsigma_k dN_k, \tag{10.5.1}$$

where $\varsigma_k = (\partial U_k/\partial N_k)$ – potential of the kth component corresponding to the osmotic diffusion of the kth substance across the system borders and therefore named the osmotic potential (V. Etkin, 1999) [1]. The first two sums of this expression characterize the independent processes of heat exchange and expansion work in a constant-composition system. They do not include the heat and bulk effects associated with introducing the kth substance and the mixing processes involved. These effects are inseparable from the substance introduction and, therefore, refer to the last term of (10.5.1).

To find a relation between the osmotic and chemical potentials, let us rearrange Gibbs' relationship (6.2.1) subtracting the terms $\Sigma_k T s_{ko} dN_k$ and $\Sigma_k p v_{ko} dN_k$ from the first two of its components and simultaneously adding them to the last component (so that not to disturb the energy balance):

$$dU = \Sigma_k N_k T ds_{ko} - \Sigma_k N_k p dv_{ko} + \Sigma_k (\mu_k + T s_{ko} - p v_{ko}) dN_k, \tag{10.5.2}$$

wherefrom it follows that

$$\varsigma_k = \mu_k + T s_{ko} - p v_{ko} = u_k - T(s_k - s_{ko}) + p(v_k - v_{ko}). \tag{10.5.3}$$

Representing the chemical potential μ_k by the known way in terms of the partial molar internal energy u_k, the partial molar entropy s_k and the partial molar volume of the kth component v_k ($\mu_k = u_k - T s_k + p v_k$) one can find that for not interacting substances ($s_k = s_{ko}$ and $v_k = v_{ko}$) the osmotic potential ς_k is equal to the molar energy u_k transferred by unit pure k^{th} substance across the system borders. Thus the thermokinetic analog of Gibbs' relationship (10.5.1), unlike (6.5.1), changes to relationship (10.5.3) for, in particular case, a single-component open system, which proves the correctness of the revision applied to the component potential expression.

Now let us consider the diffusion process in its "pure" form as a mixing of components in a system with a constant mass M and volume V, which may be both continuous and separated into two parts with a semipermeable membrane or a gate. This mixing process as well involves heat effects due to interaction between components. At V = const these

are variables s_{ko}, V and N_k that become independent, therefore the component potential is defined as:

$$\zeta_k = (\partial U / \partial N_k)_{Sko, V, Nk}. \tag{10.5.4}$$

This potential is advisably to be named diffusive. Its relation to the chemical potential may be revealed coordinating Gibbs' relationship (10.5.1) with new uniqueness conditions. Assuming in (10.5.1) $dV = 0$ and rearranging the term $\Sigma_k Ts_k dN_k$ gives:

$$dU = \Sigma_k N_k Tds_{ko} + \Sigma_k \zeta_k dN_k. \tag{10.5.5}$$

where

$$\zeta_k = h_k + T(s_{ko} - s_k). \tag{10.5.6}$$

In even more particular case, when the components do not interact and the partial molar enthalpy and entropy of the kth component are equal to those for pure substances ($h_k = h_{ko}$, $s_k = s_{ko}$), the enthalpy h_{ko} becomes the component potential. This is characteristic, e.g., for filtration process. For such processes the fundamental equation of thermokinetics in open systems becomes:

$$dU = \Sigma_k N_k Tds_{ko} + \Sigma_k h_k dN_k. \tag{10.5.7}$$

As can be seen, the variety of uniqueness conditions for processes under investigation results in a variety of component potential, which is quite naturally. From here the variety of material equilibrium conditions also ensues. In particular, at $p, T = $ const (or equivalent conditions s_{ko}, $\upsilon_{ko} = $ const) using the method described in Chapter 4 one can find that the equilibrium distribution of the kth substance among the homogeneous parts of a heterogeneous system (which parameters are single- and double-primed, respectively) occurs with the equality of osmotic potentials in them:

$$\varsigma_k' = \varsigma_k''. \tag{10.5.8}$$

Similarly, at $T, V = $ const the equilibrium condition means the equality of the diffusive potentials:

$$\zeta_k' = \zeta_k''. \tag{10.5.9}$$

At last, for a filtration process equilibrium occurs with the equality of enthalpies of the kth substance in the system and filtrate:

$$h_k' = h_k''. \qquad (10.5.10)$$

The definition of a particular form for the component potential in accordance with uniqueness conditions has far reaching consequences. Firstly, this allows finding that only motive force providing the transfer of some substance, which ceases the process if becomes zero. With such a (resultant) force found phenomenological laws (5.4.1) may be starkly simplified by negating the summation with respect to all "thermodynamic" forces $\mathbf{X}_i$ available in the system, i.e. by reducing these laws to the "diagonal" form not containing the cross phenomenological coefficients L_{ij}. Afterward this will allow reducing the number of the phenomenological coefficients in these equations, expressing the so-called superposition effects in terms of thermodynamic parameters and extending the TIP methods to non-linear systems.

10.6. Possibility of use of Environmental Heat in Non-Heat Engines

Classic thermodynamics is known to exclude using the heat dissipated from the environment in heat engines. Here the concept of the perpetual motion of the second kind as itself is rooted proposed by Nobel Prize winner W. Ostwald (1887). The ban on creation of such kind heat engines proceeds from the assumption that the environment is a heat receiver in such machines and converting it into a heat radiator in the absence of other heat receivers would mean the creation of a mono-thermal unit using the practically inexhaustible heat supplies from, e.g. the world ocean. Justice of this position is not subject to doubt.

It should be noted, however, that the equilibrium thermodynamics considered only cyclic heat engines. In such engines the working body periodically reverted to the original state, i.e. there was no exchange of substance between system and environment. Such systems have received the name of the closed.

Meanwhile in published materials quite often there are messages on working out, patenting and manufacturing of the devices using heat of environment for increase of useful work received in them (Serogodsky A, 1992; Klimov C, 1992; Buinov Г, 1992; Furriers Г, 1992; N.Zaev, 1992, etc.). There are enough of facts evidencing the increased integrity of fuel, galvanic, electrolysis, etc. devices working on the absorption of heat from the environment. Authors of managements repeatedly specified in this circumstance in electrochemistry. It is necessary therefore to show, that the principle of the excluded perpetuum mobile of 2nd sort does not concern such systems.

Let we have some device of type fuel or a galvanic cell, reformative chemical energy of any substance U_{ch} in the electric. Reversible work of such device W^e according to (9.1.8) is equal to a decrease chemical инергии systems $-\Delta E_{ch}$:

$$W^e = -\Delta E_{ch} = -\Delta(U - \bar{U}) = -\Delta U + \Delta \bar{U}. \qquad (10.6.1)$$

According to this expression, at the same initial and final condition of system ($\Delta U = $ const) work made by system decreases, if in it any processes leading to increase of anergy $\bar{U}$ (including the chemical transformations accompanied by growth of entropy) proceed. This loss of working capacity decreases, if increase of anergy $\Delta \bar{U}$ to cover not for the account of inergy, but due to external anergy sources. In particular, if reaction proceeds at $p, T = $ const, and entropy increase in it entirely becomes covered at the expense of external heat exchange, $\Delta \bar{U} = Q_0$ reversible work made by system will be equal again to a decrease inergy of systems:

$$W^e = -\Delta U + Q_0 = -\Delta E_{ch} \qquad (10.6.2)$$

However, the heat supplied to the system in this case is not converted into ordered forms of energy, т.е turns to work. It only fills up anergy increase, caused by increase of entropy of products of reaction in comparison with entropy of reagents that is peculiar to any endothermic reactions.

Certainly, the efficiency of such devices should be defined by the relation of work W^e to all spent energy of other form $E_i' = A_r + Q_0$, as borrowed the most working body ($-\Delta E_{ch}$), and brought from the outside Q_0. Therefore the efficiency of an ideal chemical element (at which $W^e = A_r$) and in this case is less than unit:

$$\eta_{ch} = W^e / (A_r + Q_0) < 1 \qquad (10.6.3)$$

This means that no laws of thermodynamics are violated herein. The understanding of that in this case a stream of heat Q_0 from environment simply compensates expenses of free energy of system for a covering of the

increasing connected energy of a working body, could come and within the limits of classical thermodynamics. However the equilibrium thermodynamics, strictly speaking, excluded from consideration internal transformation processes one forms of energy in others (including the ordered energy – in disorder). In these conditions difference from zero of circular integral $\oint dQ$ always meant transformation of heat into work and infringement of a principle of the excluded perpetuum mobile of 2nd sort.

It would seem, the understanding of an essence of processes occurring in chemically reacting environments could come with transition to nonequilibrium thermodynamics (TIP) which does not exclude from consideration internal processes and considers interrelation of diverse streams of energy. However and in this theory possibility of interrelation of the phenomena of the scalar nature (chemical reactions) with vector processes of heat exchange with environment (principle Curie) was excluded. Necessary clearness comes only in energodynamics which opens the vector nature of chemical reactions in fuel and galvanic cells, and is capable to remove not only the contradiction with principle Curie, but also the suspicious relation of an official science to any "superindividual" devices (from efficiency, big units) to which often carry also chemical elements on the ground that in them work in some cases exceeds affinity of chemical reactions.

Thus, the interdiction for use of absent-minded heat of environment in not thermal cars is caused besides by any extrapolation of principles of equilibrium thermodynamics for limits of their applicability. However inadmissibility of such extrapolation at a modern condition of a science far is not obvious.

Chapter 11.

ENTROPY RISE PRINCIPLE APPLICATION LIMITATION

Among the problems of classic thermodynamics reflecting the scientific view of the world the conclusion that heat death of the Universe is inevitable takes the high-end position. This problem has repeatedly been a hot topic both for physicists and philosophers. Overwhelming number of scientists consider this theory insolvent. However anybody yet did not manage to prove a conclusion inaccuracy in which has resulted statistical interpretation of second beginning of thermodynamics. In this chapter we will consider this question from more common positions of entrgodynamics and we will try to untangle whenever possible that ball of contradictions and errors which absolutizations of a principle of increase of entropy and to distortion of a real picture of the world have led. Basic our purpose - to show, that the reason of occurrence of the theory of thermal

death of the Universe is all the same extrapolation of thermodynamics for strict frameworks of its concepts and methods applicability that was expressed in absolutization of entropy increase principle and distortion of communication of entropy with such concepts, as "chaos", "organisation", "orderliness" and "complexity".

11.1. "Heat Death " of the Universe as Groundless Theory

According to modern astrophysics fifteen billion years of the existing metagalaxy has appeared to be insufficient for the thermal equilibrium to come and maximum entropy to be reached therein as it was predicted by R. Clausius, the founder of equilibrium thermodynamics. That prognosis was best of all manifested in his pithy phrase: "Energy of the Universe is constant, Entropy of the Universe is rising".

Clausius' contemporaries immediately traced far reaching consequences from that conclusion – from the disposition of Providence in the "Creation of the Universe" and to the inevitability of its "heat death". So broad interpretation of the entropy rise principle seemed to be extremely unconvincing to a considerable number of investigators yet in that time (J.M. Gelfer, 1979). However, despite the periodical heated discussions on the issue the entropy rise principle status has not practically changed. Therefore it is necessary to start with the very sources of the delusions that made entropy the criterion of "any and every" irreversibility.

The notion of entropy as itself was introduced by R. Clausius in connection with the necessity to find the coordinates for the reversible heat exchange process, i.e. a physical value necessarily varying in that process and ramaining invariable in its absence. This question was considered in Chapter 4, where stated that the physical sense of that coordinate should rather comply with the "thermomomentum" as a momentum of the system particles' micromotion, which has lost its vector character due to the heat motion chaotic condition. This coordinate should have retained its modest role as one of the independent arguments of the system energy. However, R. Clausius gives it a name more suitable for the energy antipode, energy "shadow", focusing thereby the attention on the entropy as a nonpersistent and arbitrarily increasing value – the property it seemed to be unique for him in that time.

As we now know, entropy is not at all the only parameter arbitrarily varying in an isolated system. According to the balance equations (2.5.8), in the polyvariant system relaxation the internal sources σ_i or sinks may essentially be attributed to coordinates (energy carriers) of any energy forms not being in internal equilibrium (i.e. for which the relaxation motive forces $\mathbf{x}_i \neq 0$):

$$\Sigma_i \int \psi_i \sigma_i = \Sigma_i \int \mathbf{x}_i \cdot \mathbf{j}_i^p \; . \tag{11.1.1}$$

Such internal sources may be, in particular, attributed to masses M_k of the kth matters, which may appear or disappear in chemical reactions, to volume V that can arbitrarily increase in the process of system expansion into void or an area with reduced pressure. They can also be attributed to parameters describing such material structure defects as number of dislocations, crystal grain size, as well as to new phase nuclei. They can also be attributed to all, without exception, moments $\mathbf{Z}_i$, describing system spatial heterogeneity and therefore arbitrarily varying in relaxation processes. Thus from the modern standpoint R. Clausius did not have enough grounds to consider the entropy as itself responsible for any irreversible processes. It should be rather explained by the fact there were no other same explicitly varying parameters for those simplest thermomechanical systems R. Clausius confined himself to when substantiated the entropy rise principle. Data on the "age" of the Universe, which could cast doubt on the fact of its tendency to thermal equilibrium, were also absent.

The probabilistic interpreting the second law of thermodynamics L. Boltzmann gave first looked like the life belt in the attempts to prognosticate a tragic fate for the Universe. According to the Boltzmann's interpretation of the second law the Universe tending to thermal equilibrium reflects just the most probable, but not at all compulsory direction of its evolution. Large-scale fluctuations – spontaneous off-equilibrium deviations associated with local entropy falls – are possible in separate parts of the infinite Universe. In such a case entropy of the Universe will rise just in average, while the world we are living in is a gigantic fluctuation. The metaphysical character of this hypothesis lies in the fact that such a gigantic fluctuation is hardly probable for its realization. The whole scope of the modern knowledge regarding the Universe evolution shows that the Universe development is a continuous complex process instantiated by the formation of stellar systems. Therefore the " today's world picture does not allow considering the development of the Universe as its transit to ever more probable states" (M.P. Vukalovich, I.I, Novikov, 1968).

The most reliable theory describing the Universe evolution is presently the "Big Bang" model based on the Einstein's general relativity theory.

The "gravitation equation" Einstein obtained within the general relativity theory referred to the Universe as a whole and assumed the space curvature $G_{\mu\nu}$ proportional to the energy-momentum tensor $\mathbf{T}_{\mu\nu}$ with the proportionality factor equal to the gravitation constant G:

$$G_{\mu\nu} = 8\pi G \mathbf{T}_{\mu\nu} \; . \tag{11.1.2}$$

According to this relation the curvature of the Universe as a whole was defined by the matter density: at a high density it was positive (as

ball surface), whereas at a low density it was negative (as saddle surface). However, Einstein, as the majority of those times-scientists assumed the University to have been stationary as a whole. Meanwhile, as A. Fridman showed in 1922, equation (11.1.20) actually did not assume stationarity: the Universe evolution character in this model depended on the matter mean density. At a high density the Universe will be collapsing, whereas at a low density it will be eternally expanding. The Universe with a critical density will be the boundary case: it will be expanding, but with a continuously decreasing rate. Hence it followed that the "geometry" and the final fate of the Universe were interconnected. A. Einstein did not agree with such a conclusion originally. However, when the American astronomer E. Hubble discovered the "red shift" of the galaxy radiation spectral lines in 1929 and interpreted it as the consequence of the galaxies' "recession", Einstein acknowledged the Fridman's rightness. The further measurements made for the expansion rate of the galaxies showed that the Hubble's time ("Universe age") had the order of about just 15–20 billions years. In this context a real battle deployed in asrophysics to defend certain world outlook systems. Evolutionists believing that the matter is developing without any "interference of Providence" considered the Hubble's time a hopelessly short period for atoms to transmute into living being. Creationists (advocates of the "young" Universe) based on a free interpretation of the Bible, on the contrary, insisted on the time of the Universe formation as just 6-10 thousands years ago. A good many investigators spent incredible amount of energy and effort in their attempts to reconcile these concepts.

R. Tolman based on thermodynamic ideas assumed in 1922 that at the moment of its "origin" the Universe featured extremely high temperatures. It was the same conclusion G. Gamov came to in 1946 when clarified the temperature conditions required for beginnings of the variety of elements in the Universe, which we observe today. That served as the basis for the "Big Bang" concept stated that the whole Universe had appeared from the "singularity" – infinitesimal volume that contained the entire mass of the future Universe with infinite (or close to infinite) values of density, temperature and pressure – as a result of the extremely fast expansion. This theory has till now remained most recognized though, in opinion of a number of astrophysicists including the Nobel prize winner C. Alven, is an "outrage against common sense".

Lets start from the fact that the advocates of the "Big Bang" concept, though acknowleging the second law of thermodynamics with regard to the inevitable "heat death" of the Universe (and hence its "commencement") at the same time bypass the glaring contradiction between the second law above and the energy concentration before the "Big Bang". According to this law a system can be withdrawn from equilibrium with

the environment only by having done a certain external work. However, the energy source required for this is knowingly absent in the "void" surrounding the Universe. This fact alone is quite enough to reject any arguments in favor of the "Big Bang" theory. However, this theory exists and is well recognized as a "firmly established fact". Therefore we have to once again apply to the *processes' counterdirectivity principle* proved in Chapter 1. Let us consider the Universe in whole as a closed system occupying the entire conceivable space V. Mass M of such a system remains invariable in time t, i.e. $\partial M/\partial t = 0$. Representing M as the bulk integral $\int \rho dV$ of the system density ρ gives for the system as a whole:

$$dM/dt = \int(\partial\rho/\partial t)dV = 0. \qquad (11.1.3)$$

This integral being equal to zero may take place in only one case – when the sign of the derivative $(\partial\rho/\partial t)$ is opposite in various domains of the system. This means that whereas density increases in some domains of a closed system (compression), it decreases in other domains or bulk elements (expansion). This means that allowing for the counterdirectivity of processes is compulsory for any theory pretending to generality, including the Einstein's theory of the Universe evolution as well.

One of the basic questions is whether the process nonstationarity in the Universe may be a ground to assert its boundaries are nonstationary. The answer to this question becomes especially clear from the positions of the principle proved above. From this principle it follows that processes inevitably appear in the Universe and run simultaneously as expansion in some of its parts and as compression in others. These are such processes that lead to mass concentration in certain parts of the Universe, stellar clusters therein, accretion, collapse, "supernovas" followed by matter dissipation and clustering in other parts of the Universe. This *dichotomy* results in inadmissibility to consider the Universe as a homogeneous system, which evolution direction entirely coincides with that for any of its parts. Therefore equation (2) should be rewritten as integral with due consideration of the variable density for the energy-momentum tensor $\rho_{\mu\nu} = \partial\mathbf{T}_{\mu\nu}/\partial V$:

$$G_{\mu\nu} = 8\pi G \int\rho_{\mu\nu}dV. \qquad (11.1.4)$$

Hence it follows that according to the analysis of the Einstein's equation given by A. Fridman the behavior of the Universe in its separate domains will be different against their density: it will shrink up to collapse in high-density domains, whereas expand in low-density domains. Thus the nonstationarity of the Einstein-Fridman's model of the Universe should be construed not as expansion or constriction of its boundaries,

but rather as inconstancy of parameters in its internal domains, i.e. in strict conformity to this notion content. Such an interpretation not at all contradicts the infinity of the Universe and absolutely corresponds to the ideas of the "pulsing" Universe Indian and later Roman philosophers adhered to yet thousands years ago.

The "Big Bang" concept coming into conflict with the processes' counterdirectivity principle becomes especially clear when using such arguments as the "red shift" since the recession rate of galaxies, according to measurements, is the same in all directions. This is equivalent to the statement about the absence of the processes opposite to the "recession" of galaxies. However, such a "narrowness" of processes is absolutely in the spirit of the entropy rise principle. Therefore it is of interest to clarify how the entropy S as one of the independent arguments of the Universe state function has turned into the general measure for degradation of all forms of the Universe energy (kinetic, gravitational, chemical, radiant, thermal, intra-atomic, intranuclear, etc)?

11.2. Failure to Prove Entropy Rise Principle

The question is quite natural: whether there are strict and general proofs of the entropy increase law ? In chapter 4 we have discussed by consideration of classical thermodynamics from energodynamic positions an inconsistency of proofs of Clausius' principle of increase of the entropy, based on comparison of thermal efficiency of reversible and irreversible thermal cars, and it is offered new, energodynamic proof of a principle of increase of entropy. From it followed, that entropy increases only in the processes of dispersion of energy when the final form of energy is heat. Let's show now, what is it correctly even then when the initial form of energy is all the same heat. As experimental acknowledgement of such transformation mentioned in a part 1 «the effect of growth measured enthalpy» (L.Brovkin, 1960, 1964). The increase found out in him of mean temperatures of the sample (a rolled paper, a cardboard, rubber) in the course of alignment testified to transition of the ordered part of thermal energy $E_\text{т}$ in disorder $\bar{U}_\text{т}$ in the course of a system relaxation. The same phenomenon is observed at irreversible heat exchange in thermally non-uniform environment, formed to M.Planck by a basis of one of the most convincing proofs of a principle of increase of entropy. It has considered thermally non-uniform isolated system which consists of two homogeneous subsystems with temperatures T_1 and $T_2 < T_1$, exchanging among themselves warmth Q. Having designated entropy of the first and second subsystems accordingly through S_1

and S_2, it has found, that elementary quantities of heat given by the first subsystem and perceived second, are equal accordingly:

$$đQ_1 = T_1 dS_1 < 0; đQ_2 = T_2 dS_2 > 0. \qquad (11.2.1)$$

From here follows, that in force $đQ_1 = - đQ_2$ change of entropy of all system as a whole dS is positive:

$$dS = dS_1 + dS_2 = đQ_2/T_2 + đQ_1/T_1 = đQ_2(1/T_2 - 1/T_1) > 0. \qquad (11.2.2)$$

Thus, thermal energy, as well as any its other forms, is capable to dissipation and is not purely chaotic as it is considered to be. Hence, it is necessary to specify, that *entropy increases in all processes in which the ordered forms of energy turn to disorder thermal energy.*

However from here yet does not follow, that also other forms of disorder works thus do not increase. As follows from the equation of balance (2.5.8), in processes of a polyvariant systems relaxation internal sources σ_i can exist basically at any forms of energy which are not in balance $(x_i \neq 0)$:

$$\Sigma_i \int \psi_i \sigma_i = \Sigma_i \int \mathbf{x}_i \cdot \mathbf{j}_i^p . \qquad (11.2.3)$$

Such internal sources are available, in particular, for mass of kth substances M_k which can arise or disappear during chemical reactions, at volume V which can increase spontaneously in the course of system expansion in emptiness or area with the lowered pressure. There are they and for the parametres characterising such defects of structure of materials, number of dispositions, the size of crystal grains, and also at germs of a new phase. There are they and at all without an exception of co-ordinates $\mathbf{Z}_i$ spontaneously changing in processes of a relaxation. Therefore from the modern point of view R.Klauzius did not have sufficient bases to consider entropy responsible for any irreversible processes. More likely it has been caused only by that the elementary thermomechanical systems to which R.Klauzius was limited at a substantiation of a principle of increase of entropy, there were no other spontaneously changing parametres.

That fact, that quantity allocated at dispersion of heat energy $Q^{\text{Д}}$ appears more often less than work of dispersion $W^{\text{Д}}$, testifies that in these processes the part of the spent energy has passed in internal energy of crystal structure, in superficial energy of a powder and other not thermal forms of energy. It means, that transition of the ordered forms of energy in thermal is not a unique consequence of dispersion of energy. It was re-

vealed experimentally on a difference of isothermal heat of dissolution of the initial and deformed material [1]. Thus, entropy transformation into "whipping boy" as unique measure of dissipative losses is a consequence all of the same extrapolation of conclusions of classical thermodynamics on polyvariant systems. This is especially evident from the positions of energodynamics, according to which entropy varies only with the variation of the "bound" (or internal heat) energy of a system. It does not matter in this case why this energy varies – either due to the system heat exchange or because other ordered forms of energy spontaneously are converted into it. Dissipative function expression (5.3.3) in the theory of irreversible processes clearly reveals the failure of attempts to prove the thermodynamic entropy rise in irreversible processes having nothing to do with appearance of internal heat sources (wells). Thus, entropy transformation into "whipping boy" as unique measure dissipativnyh losses is a consequence all of the same extrapolation of conclusions of classical thermodynamics on polyvariant systems.

It is impossible within the framework of this book to adduce all arguments to prove that the absolutization of the entropy rise law can not be justified by considerations of the physical character. Therefore let us just refer to a conclusion one of the famous investigators of the thermodynamic principles, K. Putilov (1971), made, *"In classic and the last investigations on thermodynamics we do not find a statistics-independent, perfectly rigorous proof of the thermodynamic inequalities (except, may be, the reasoning Planck developed [1]). As for the inequalities just thermodynamically derived from unattainability of the perpetual motion of the second kind or from other sweeping enough statements of the second law of thermodynamics, those appeared to have often been so non-rigorous that many authors were disposed to see an incurable logical drawback in this part of thermodynamics. This explains why a number of solid manuals deny the possibility to prove the entropy rise theorem as purely thermodynamic and statistics-independent"*.

As we now start to guess, the general proofs of this principle within the limits of classical thermodynamics are not present and cannot be on the merits of case. Let's imagine any thermomechanical system, which energy U is function of entropy S (or temperatures T) and volume V, i.e. $U = U(S, V)$. Then, considering entropy as inverse function $S =$

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[1] This is the way, e.g., the difference between heat capacities of a strained and unstrained spring is revealed

[1] This case pertains to the process of thermal relaxation of two subsystems with different temperatures, where inergy of a thermally heterogeneous system changes to anergy in strict compliance with energodynamics.

S (U, V), we will find, that for the isolated systems (U, V = const) which the principle of increase of entropy concerns, entropy cannot change, as invariable there are all arguments of this function. Physically it is obvious enough: in equilibrium system there can not be the processes of the relaxation leading to transition of ordered energy in the chaotic. It the conclusion made K.Putilov (1971): *«inequalities for entropy are unconditionally recognised for a long time not because they have been strictly proved within the limits of the macroscopical physics, and that is why, that to them as to an inevitable conclusion, has resulted statistical interpretation of 2nd beginning of thermodynamics».* Such point of view compels us to address to statistical proofs of this theorem.

11.3. Nonidentity of Thermodynamic, Statistical and Informational Entropies

One can hardly find one more concept in the world literature, which would give raise to the same amount of disputes, loose talks and insinuations as entropy. Tens of books and hundreds of articles have been dedicated to entropy. This concept has long outstepped the borders of physics and penetrated into the inmost of human mind. The statistical, informational, mathematical, linguistic, etc. entropies have appeared. Truth and errors have been so deeply intertwined that it is practically impossible to date to get to the historical, epistemological and pragmatic roots of this concept. Besides, no alternative to entropy made the job a blind alley. Only introducing the concept of ynergy as an analog of the Gibbs' free energy – more universal, physically more evident and more feasible – engendered hope to once and for all loose the fetters of entropy misreading.

As shown in Chapter 4, entropy is just one of the independent state coordinates, which serves as an extensive measure of random momentum in a system. This value relates to the Helmholtz bound energy TS in the same manner as the ordered momentum $M\mathbf{v}$ with its work-kinetic energy $\mathbf{v}^2$ (double kinetic energy). The random momentum value varies in only the thermal process[1], whereas the system energy – in any processes running in the system. The internal thermal energy U_T or the bound energy TS varies due to the heat Q supplied from outside or the dissipation heat Q^d released in the system. However, the Q^d releasing and the associated entropy rising is just a part of the state variations caused by the energy dissipation. In particular, when metals are cutting or hard material crush-

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[1] Remember that the thermal process is understood, after K.M. Putilov, as a process involving the internal thermal energy variation (see Chapter 3).

ing, a part of the work herein done is consumed for the destruction of the materials and for their surface (potential) energy variation. As a result, the heat output ratio (the heat released related to the work done) in such processes appears to be less than unit. Hence, the dissipation of energy (reduction of its free (reversible) part) may exceed the amount of the heat released and is not therefore defined by only the entropy rise. The issue of entropy as one of the parameters rising with energy dissipation should seem to be closed here. However, in 1911 Boltzmann, who did not wish to make up his mind to the inevitable "heat death of the Universe", proposed other substantiation of this principle. That proceeded from the assumption that the entropy rise in irreversible processes reflected the tendency of nature toward a more probable state. In case of ideal gas with non-interacting particles this corresponds to such their velocity distribution, which is realized by the most of means (i.e. most probable). Then the relationship between the entropy S and the said "thermodynamic probability of state" $\hat{W}$ has the form:

$$S = k_{\text{Б}} \ln \hat{W}, \qquad (11.3.1)$$

where k_{B} – constant subsequently named after Boltzmann.

According to this expression the entropy of thermodynamic systems is proportional to the logarithm of probability of their state $\hat{W}$. When having derived expression (11.3.1), the main assumption was that the most probable distribution of particles was at the same time equilibrium one. That was based on the fact that both said values (entropy S and thermodynamic probability of state $\hat{W}$) were additive and reached an extreme in equilibrium state. Since the maximum $\hat{W}$ is associated with the "molecular chaos" state, the entropy in the Boltzmann's concept has been construed as a measure of the system state disorder. As a result, it has been converted from the reversible heat exchange coordinate into a global measure of "chaos". The development of this concept has led to the entropy in a number of up-to-date theories being attributed to not only the Universe, but even to objects not at all having the heat form of motion, including the physical vacuum.

In this connection the question is quite natural, to what extent the Boltzmann's principle is sound as stating the proportionality between the entropy and the state probability logarithm. These two values being correlated does not mean at all these are related via a unique dependence of the (11.3.1) type. Entropy is after all not the only value spontaneously varying in one direction. Many of the independent coordinates Θ_i vary in the same way in an isolated system, as well as such functions of state as the Helmholtz Γ and the Gibbs G energies, which much more profoundly reflect the variation of a state than the bound energy TS. Besides, these,

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unlike entropy, vary in the same direction with the Boltzmann "collision integral". These are parameters that should seem to be related to the probability of state rather than the entropy as one of the arguments of these characteristic functions. Broadly speaking, there are a lot of questions to be asked of L. Boltzmann (P. Chambadal, 1967). All of them evidence that entropy has become a probability measure just on subjective accounts.

We will not discuss here the question to what extent the phenomenological (i.e. experience-based) thermodynamics may be "substantiated" by the methods of statistical mechanics proceeding from a number of hypotheses "containing much vagueness" (R. Kubo, 1968). We will not either explore how close to the primary principles of thermodynamics the "Boltzmann principle" lies, which identifies the thermodynamic entropy with the state probability logarithm, as well as to what extent those assumptions are correct the Boltzmann statistical entropy is based on. Let us just note the differences in their physical meaning and behavior. To start with, the entropy in thermodynamics is a carrier of the heat form of motion, i.e. the value that can be transferred across the system borders in course of the heat transfer or mass transfer between the system and the environment. This fact is reflected in thermodynamics of non-equilibrium processes as the concept of an "entropy flow" similar to the substance flow, charge flow, etc. It is absolutely senseless to speak of a "state probability" transfer across the system borders. Furthermore, as the math modeling of mixing processes shows, the tendency of the particle distribution probability toward rising appears in this process yet at a number of molecules equal to or exceeding three at an arbitrary small interaction between them, i.e. at the conditions quite irrelevant in application to a thermodynamic system. Therefore, the fact itself the most probable state has been reached is not yet a sufficient evidence of thermodynamic equilibrium. In other words, equilibrium and chaos are distinguishable notions. A special part is assigned here to metastable states which do not correspond to the probability maximum being an equilibrium state variety, though.

Different behavior of the thermodynamic and statistical entropies may be additionally instantiated by also the spontaneous ice crystallization in supercooled liquid or by the precipitation in oversaturated solution involving its structure ordering (i.e. Boltzmann and Gibbs entropies decrease) and, at the same time, temperature rise and thermodynamic entropy increase. Scientists from Fourier University and ILL (Institut Laue-Langevin, Grenoblois, France) have recently obtained a substance that solidifies when heated and melts when cooled, i.e. behaves exactly opposite to the statistical entropy. At last, when placing a system in the field of external potential forces, its state as well becomes more ordered, whereas

the thermodynamic entropy remains unvaried at that (due to the adiabatic action of these forces). The difference between the thermodynamic and statistical entropies shows also at estimation of their values by the temperature of the relict radiation filling the Universe. The statistical temperature of this radiation found by the average velocity of cosmic particles' motion exceeds 2,000 K, whereas the thermodynamic temperature found from its spectral characteristics is below 3 K. Thus quite enough experimental facts have been accumulated up to date evidencing that the thermodynamic entropy and the statistical entropy are far from being the same notion.

Even further in its physical meaning the informational entropy stands, which was introduced by Shannon (1949), as many investigators suppose, just "due to a careless application of this term". He found that the volume of information obtained from measurements on a system was related to the associated state probability variations of the system via the same relationship (up to a sign) as for the statistical entropy. This formal likeness between the thermodynamic entropy expression and the information volume decrease led him (and after Brillouin (1955) – also other investigators) to their groundless identification.

In fact, the notion of information is ambiguous and even now is still in the making. One of its early definition is semantic and means a new knowledge obtained from outside. This definition is rather subjective as the volume of information in the same message is different for people with different knowledge. Fisher endued this notion with quite other meaning utterly excluding the semantic (notional) matter from consideration. The information by Fisher is associated with the math expectation of indeterminacy evaluation and mathematically expressed by a negative logarithm of probability of an experimental outcome (the higher the expectation of whatever experimental result, the less the new information that can be taken from this result; and vice versa – the higher the entropy S of the information source, the more the information can be obtained from it). The information by Shannon is another kind of information construed as the probability to obtain reliable information via some communication channel allowing for inevitable interference. The fourth kind of information is the information by Brillouin named also "structural" or bound information. This is construed as the difference between the entropies S of a system in its current and equilibrium states, i.e. the "deficit" of the entropy as compared with its maximum value in equilibrium state. It is this structural information that is associated with the notion of informational entropy as a measure of indeterminacy of our knowledge about the system. Note that unlike the previous definitions characterizing the information as the function of a process (cognition, experimental data acquisition, information transfer, etc.) the structural information stands

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closer to the function-of-state concept thermodynamics operates. Actually, the higher the system organization level (i.e. the further the system stands from equilibrium), the greater the future increment of its entropy as it is approaching equilibrium (i.e. the entropy deficit). In this sense the structural information transfer to the system is someway or other associated with its ordering, i.e. with doing work on it. In this case the informational entropy is just an ineffectual substitute of the free energy or the useful work concepts in thermodynamics.

Thus the application range of the term "information" is very wide – from a measure of some system elements' degree of order to the contents of the signals a creature perceives from the outside world. The informational entropy is generally associated with the information acquisition process and is not the state parameter unlike the thermodynamic entropy. As a result, the investigators, who examined the case more closely, have come to a conclusion that those two entropies, despite their affinity, are evidently distinguishable, and their identification may proceed just from lack of understanding. Anyway, using the same term (entropy) for different values just misleads (I.P. Bazarov, 1991).

The statistical - informational treatment of entropy has led to occurrence of its antipode - "negentropy" (negative entropy). For the first time this term has applied L.Boltsman at statistical treatment of concept of entropy. On L.Boltsmanu, process of a transmission of energy from the Sun to the Earth means redistribution between them entropy with subsequent "ordering" of Earth. From here it makes a conclusion, that struggle of biosystems for existence is a struggle for negentropy, instead of for raw materials and free energy. After this E.Shredinger (1944) writes about "to delivery of negative entropy with a sunlight" and about "vysasyvanii" its(her) organisms from environment.

This idea was then is picked up by I.Prigozhin (1980, 1986) and its followers explaining existence of stationary conditions by a supply of negentropy. It seemed to them, that receipt "negentropy" allows to explain the phenomena of "self-organising" occurring in the nature. This concept was extended and in synergetrics. Meanwhile such "explanation" encounters serious contradictions. First of all, entropy receipt in an organism with a foodstuff exceeds, as a rule, its removal with ability to live products (ekskriments). As to removal of entropy by heat exchange, that it is practically absent at cold-blooded animals and fishes, and also cannot serve as the receipt reason of " negentropy". Thus, attempts of researchers to explain the structural organisation and functioning of organisms and their communities not a supply of free energy, and receipt of negentropy appear in actual fact insolvent.

At last, the concept of negentropy is in a glaring contradiction with thermodynamic principles of a state co-ordinates finding, since in it all of

them are sizes especially positive (as well as energy which each of them defines for lack of other degrees of freedom). Therefore the remark is absolutely true that the question regarding the physical grounds of the monotonic entropy rise remains … still open" (L. Landau, E. Livshits, 1973).

11.4. Ambiguous Relation of Entropy with Irreversibility and Dissipation

First S. Carnot in his "Réflexions…" (1824), then R. Clausius in "The Dynamic Theory of Heat" (1850) showed by different ways that if a heat engine was arranged so that in its reverse-direction operation all mechanical and heat effects were converted into their inverses, the engine would do the maximal amount of work. That meant that "the mechanical energy thus expended might be returned to the initial state" (R. Clausius, 1950). Thus the concept of reversibility as a possibility to return a system to its initial state appeared immediately having taken the character of an initial postulate. From how this term was applied, the classicists construed it as a possibility to recover the "motive force of heat". In particular, W. Tomson in his article "On Dynamic Theory of Heat" directly writes, "When heat or work is obtained with irreversible process, the dissipation of mechanical energy occurs and its complete return to the initial state is impossible". Since the mechanical energy is measured by the amount of work that a body (system) can do, the irreversibility, as the founders of thermodynamics understood it, was a synonym for loss of capability to do work by the body (or, as we term it now – "dissipation" of energy).

However from here yet does not follow the return conclusion, that any irreversible process is dissipation. In particular, establishment process maksvell-boltsman's distributions on energijam noninteracting particles is irreversible, as it is necessary to spend work for their division. Meanwhile this process is not accompanied by heat allocation, i.e. energy dispersion. Further, as will shown in chapter 12, process of mixture of the noninteracting gases, which are at identical temperature and pressure, is also irreversible. But it is also not accompanied by working capacity loss, as the system of noninteracting gases even before mixture was in full (thermal and mechanical) equilibrium [1]. The similar situation arises and in the example resulted above drosselirovanija ideal gas in the thermal machine. This process is irreversible also, but in the conditions of experience, when in the machine is used only thermal energy of a heat source, instead of its potential energy, it does not call decrease in thermal efficiency and loss of power of the thermal machine. Expression (4.3.4) re-

flects it with all necessary generality, showing, that entropy increases only in the processes connected with occurrence of internal sources of heat. The understanding of it compels to concern the maintenance of these concepts more attentively.

Irreversibility has long become the "stumbling block" for many of physicists and philosophers. Some of them consider it to be a result of the interaction of a great number of reversible elementary processes, some ascribe it to the irreproducibility of boundary and initial conditions, some – to the non-commutativity of measurement procedure and impossibility because of it to return to initial state, some – to the disturbed symmetry of physical laws at a time sign variation, others – to the statistical nature of time, etc. Meantime, R. Clausius and W. Thomson, the founders of thermodynamics, construed the irreversibility just as a result the system lost its capability for work (efficiency reduction in heat engines). This irreversibility ensues from the dissipation of energy with its ordered forms changing to heat. Any dissipative process of such kind is irreversible insofar as the "dissipated" heat can not be completely converted into work. We will refer to such irreversibility as thermodynamic one. These are just the irreversible processes the entropy rise law applies to in thermodynamics.

The irreversibility involving the "path branching" (K. Denbigh, 1989) is another kind of irreversibility. This kind of irreversibility resembles a growing tree, which trunk is a system with the only degree of freedom, while the branches – a multitude of the paths for the polyvariant system development. When a system has the only degree of freedom, all the processes running therein are caused by the only motive force. In such a case to return the system to its initial state, it would be enough just to reverse the sign of this single force. However, according to the theory of irreversible processes, to enable running some nonstatic process in a system with many degrees of freedom, all thermodynamic forces of the same tensor rank available in the system have to be overcome. Here, depending on the nature of the forces being overcome (mechanical, electrical, chemical, surface, magnetic, etc) processes occur involving the energy conversion into not only heat, but also other forms of energy. In such a case the sign reversal for motive force of any of these processes will not allow returning to the process start. To do this, the reversal of both sign and magnitude for all thermodynamic forces being overcome in the direct process will be necessary. It is impossible in the general case since in any reverse process the same "path branching" as in the direct process is observed. As a result, instead of one line we get ever more tangled web of such lines. Owing to this, the polyvariant systems subjected to action of many forces can develop irreversibly (i.e. one-sidedly) never returning to exactly initial state. This is the development of the Universe according to the modern views.

Furthermore, the irreversibility may be a result of the limit transition to infinite number of particles due to impossibility to reconstruct their initial distribution. Lastly, the irreversibility may appear in an infinite-size system, as the Universe, because a "signal" does not return to the system or returns with a delay.

Thus the current concept of irreversibility is much wider than its interpretation by Clausius and Thomson. That philosophical amplitude and sounding was added to the irreversibility concept by M. Planck, who construed it as the "impossibility to return entire nature to the state it had been in to the moment the process started up" (M. Planck, 1935). Various aspects of the irreversibility issue run into one in this his statement. From a scientific standpoint all processes are irreversible which follow the cause-effect chain since effect can not engender cause. From a statistic-mechanical standpoint all processes are irreversible which increase the state probability. From the positions of the theory of information all processes are irreversible which involve reducing the determinacy of our knowledge of a system state. In thermodynamics all processes are irreversible which lead to the conversion of ordered forms of energy into heat. The scope of these concepts is very ample. Therefore it should be distinguished a thermodynamic irreversibility due to the thermodynamic entropy rise, a statistical irreversibility due to the statistical entropy rise, and an informational entropy due to the informational entropy rise. This is a medley of these aspects of irreversibility and associated concepts of entropy, where the errors are rooted, which have led to the absolutization of the entropy rise law and to the conclusion of the inevitable "heat death of the Universe".

So, the interpretation of entropy as antipode of "organization", "order", "complexity", etc., has not only distorted the true relation of this concept with the irreversibility and dissipation, but also led to an incredible mishmash of notions. This mishmash has caused a number of paralogisms in thermodynamics. Some of them are considered in this book.

Let us show now that reaching the most probable state is not yet the sufficient criterion of thermodynamic equilibrium. In other words, we will attempt to clarify how far the "Boltzmann principle" identifying entropy with the state thermodynamic probability logarithm and equilibrium – with chaos corresponds to reality.

Yet in the ancient doctrines equilibrium was construed as a neutral position between the forces of "order" and "chaos" excluding the possibility for any of them to prevail. The medieval and later doctrines of ethics and morality used a term of "equilibrium of thought" where consequences from general principles conformed to particular cases. In mechanics equilibrium has been understood as a state where the sum of forces and moments acting on a body is equal to zero. In chemistry it has

been a state where the rates of direct and reverse reactions are equal. Thermodynamic equilibrium has been defined as a state where any macroprocesses cease with system parameters remaining invariable. In economics equilibrium means a situation where all the factors influencing, e.g., the price of a good completely balance each other remaining the price untouched. In natural science and sociology equilibrium has always meant a balance between animate and inanimate natures. The notion of equilibrium appears even in the games theory meaning there a single strategy for all partners. All this complicates a general definition of the notion of equilibrium. The encyclopaedia gives the most general of the definitions: equilibrium is such a state of a system when all the forces acting on the system are mutually balanced.

It seems that should equilibrium be the resulting action of forces, it ought to be expressed in terms of forces as adopted in mechanics. However, absolutely other situation has primordially emerged in classic thermodynamics. Thermodynamics by Clausius allowing the possibility of energy exchange in the absence of forces had to look for other equilibrium criteria and has found them as the conditions of entropy maximum. Let us now clarify how far such an interpretation of equilibrium corresponds to the notion of "chaos" and the Boltzmann principle.

There is no a general definition for the notions of order and chaos, which are the same ancient and mystic as the order and chaos themselves. Only recently a hope has appeared to examine how these notions interrelate with the entropy, irreversibiliyt and evolution. This hope is based on the development of computational methods for analysis of nonlinear systems, which allow in-depth understanding of how the unpredictability mechanisms work including the two-sided transitions "order – chaos" and "chaos – order".

When opposing "chaos" to "order", the former is usually construed as disorder, chance, unpredictability, etc. These terms are usually applied as almost synonyms despite the evident difference in their contents. Meanwhile, it is necessary to clearly discern what these terms are referred to – either state or process. If to state, then the criteria of chaos should be construed as indeterminacy of position, momentum and energy of each of the particles comprising the system. If to process, then the criteria of its stochasticity should be construed as unpredictability of this process character, i.e. its path in the space of those variables that define the state of the above parmeters and thereby – the direction of evolution for the system as a whole. These notions (state and process) are so different that their confusion can proceed from just misunderstanding.

Meanwhile, L. Boltzmann, when defining entropy as a state function, means, nevertheless, the process of rearrangement of particles realizing this state, which features the unpredictability of position and momentum

for each separate particle. Thereby the notions of "disorder" and "chaos" as referred to *process* actually apply to the *state* parameter.

Let us show now that the statistically definite state of a thermodynamic system is not at all chaotic. First of all, the condition of thermal, mechanical, chemical, electrical, etc equilibrium for two and more parts of some thermodynamic system is understood as the equality of corresponding parameters therein (temperatures T, pressures p, chemical μ, electrical φ, etc potentials). This corresponds to the uniform distribution of these parameters over the bulk of the system, i.e. to a certain macrostate order. Furthermore, there is a quite definite (maxwell-boltzmann) velocity distribution for particles in the thermal equilibrium state. The principle of equal energy distribution per micromotion degrees of freedom is a certain order manifestation, too. This property of equilibrium states has been recently called the "equilibrium order".

With the developing theory of irreversible processes in heterogeneous (spatially nonuniform) systems the idea of the "nonequilibrium order" has also appeared. The notion of "kth order stationary state" is one of its manifestations. According to the I. Prigogine's theorem (1947), with decreasing number k of the thermodynamic forces $\mathbf{X}_j$ supported from outside the force-associated fluxes $\mathbf{J}_j$ disappear. In this case the power of dissipative processes decreases, and the system spontaneously changes to a stationary state of less order (featuring less entropy generation dS/dt) untill it finally reaches the zero order stationary state – thermodynamic equilibrium. Paradoxical situation has arisen – the more appreciable dissipation (i.e. system tendency to "chaos"), the higher stationary state "order !

This paradox can be eliminated in energodynamics by finding the forces $\mathbf{X}_j$ on a more general basis as the derivative of the system energy E with respect to the corresponding coordinate of the relaxation process (5.2.1) rather than from the entropy generation expression (5.1.4). Then it will appear that the so-called stationary states are the incomplete equilibrium states featuring the cease of the corresponding process. In such a case it will become evident that for a system with n degrees of freedom the cease of k processes out of n those possible means the equilibrium of the k/nth order, i.e the less order than at complete equilibrium ($k = n$). Thus the system being further from the thermodynamic equilibrium state, the higher efforts should be exerted to keep the "nonequilibrium order" in the system.

We will show hereafter that all the so-called "superposition effects" described in thermodynamics of irreversible processes as a result of the corresponding order stationary state are actually the partial (incomplete) equilibrium states featuring the cease of one or several processes running in the heterogeneous system.

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Here comes, in particular, the pressure distribution in the gravitational field of the Earth known as the barometric height formula. In the case of material equilibrium of heterogeneous systems a quite certain regularity in the concentration distribution for diffusing components is observed. In a similar way a quite certain velocity profile arises in the turbulent (chaotic) flow of liquid and gas. Moreover, one more regularity is revealed: the energy distribution per turbulent pulsations frequency appears to be proportional to the wave number in the –5/3rd power (law of five third). Even in the Brownian motion considered as a classic example of stochastic process a certain regularity has been successfully revealed with regard to the mean free path (Einstein's formula).

Thus equilibrium may be by no means identified with chaos. This is valid for all kinds of equilibrium – true and constrained, complete and partial, external and internal, stable and labile, thermal and mechanical, chemical and electrical, osmotic, etc.

11.5. Inadequacy of Evolution Entropy Criteria

Looking back at the historical past one can hardly refrain from bewilderment on the occasion on how entropy S as one of the independent arguments of the characteristic functions describing thermodynamic system state has turned into the criterion prognosticating the fate of the whole Universe. Indeed, to describe the behavior of a system featuring far greater number of degrees of freedom than the thermodynamic system and being, in addition, unrestricted in space and time, it would be necessary to know, at least, the general form of the state equation connecting the energy of such a system with its arguments. Even confining oneself to the parameters known from energodynamics the equation of its state will look like a function of a whole number of coordinates $U = U(\Theta_i, \mathbf{R}_i, \boldsymbol{\varphi}_i)$. The number of such coordinates in each group of processes (uniform, redistribution and reorientation) can be unlimited ($i = 1, 2, \ldots, n$). Imagining the entropy S of such a system as a reverse function of the remaining variables $S = S(U, \Theta_{i-1}, \mathbf{R}_i)$ including the system energy U, it becomes evident that entropy in isolated systems ($U = $ const) can vary in only the case when some other parameters Θ_{i-1}, $\mathbf{R}_i$ have internal sources (i.e. vary spontaneously). However, in such a case there is no need in entropy any longer since the role of this function in each particular case can be played by a corresponding parameter.

In such a situation not entropy as one of the independent energy arguments evidently becomes the preferred criterion of system evolution, but any of the characteristic state functions depending on all arguments and not featuring the conservation properties. Here come, in particular,

the Helmholtz and Gibbs energies. It is regrettable that the founders of thermodynamics and their followers have chosen other way.

It is difficult to find a lamer criterion of evolution among the known thermodynamic parameters than entropy. Indeed, the thermodynamic entropy (as any other one pretending to adequacy to it) is known not to vary in reversible adiabatic processes. In other words, it does not vary exactly when the system ordering occurs, which, according to classic thermodynamics, is possible only with external work done on it against equilibrium! It does not vary either when the in-system ordering processes ("structure formation", "self-organization", "self-assembly", etc) are running as a result of internal processes of converting some ordered forms of energy into other ones should they be so perfect as to run without losses. Even with losses available, to assess the process perfection degree, the work value causing this ordering should be known. In such cases using entropy is equivalent to the attempt to evaluate the process efficiency by only the loss value without knowing the process productivity. It is tantamount to the assessment of the labor quality by the amount of sweat the worker exudes!

Strictly speaking the entropy maximum is as well inapplicable to solution of even simpler problems. Earlier, when considering the equilibrium conditions (Chapter 4), we mentioned that the equality of temperatures, pressures, chemical etc potentials was a consequence of two assumptions. Firstly, Gibbs assumed as "evident" that the variations of the internal energy U, volume V and any other thermostatic coordinate Θ_i in any part of a system are independent. However, according to the "caloric" equation of equilibrium system state $U = U(T, V, \Theta_i)$ the system internal energy is a function of parameters for all degree of system freedom and, to consider it as independent variable, the conditions enabling this should be specified. Gibbs evidently considered this fact as superfluous. Meanwhile, the ways to maintain the energy U of any subsystem at its temperature and pressure variation are not found yet. The forced maintaining of them (stationary state) means the impossibility to establish thermal and mechanical equilibrium. Secondly, the application of the entropy maximum criterion leads, generally speaking, to the equilibrium conditions in the form

$$\Psi_i' / T' = \Psi_i'' / T'', \qquad (11.5.1)$$

but not to equations (4.6.8) and (4.6.9). This means that the Gibbs-found conditions of mechanical and chemical (material) equilibrium require thermal equilibrium preliminarily established (from here comes the conclusion of a special role of this equilibrium). However, when considering hereafter the transfer processes in multi-component systems, we will see that the duffusion of one of the components may cease also in the absence of thermal equilibrium, including the case when the volume of

the subsystems vary due to the diffusing matter transfer (Kirkendall effect). Otherwise, we would be at all deprived of the possibility to refer to the mechanical, thermal, chemical, etc types of equilibrium as its independent types despite the statements of Gibbs himself.

Furthermore, using the entropy rise principle $dS/dt > 0$ in the theory of irreversible processe leads to the necessity to deny the notion of incomplete (partial) equilibrium and to replace it by the notion of "the kth order stationary state". This is how the polyvariant system state is called in this theory, when only a part of the parameters is maintained from outside as invariable, while the other processes cease. If based on only the entropy rise principle, the kinetic equations for irreversible processes in such systems take the form of the Onsager laws (5.1.6). It follows from them that the condition for some ith process to cease (flux J_i disappears) for any pair of the dissimilar forces X_i and X_j is expressed as:

$$L_{ij} X_j = - L_{ii} X_i. \qquad (11.5.2)$$

These expressions do not contain the equality of the forces X_i and X_j, i.e. equilibrium. What follows from them is only the relation between forces, which is expressed in terms of the kinetic coefficients L_{ii} and L_{ij}:

$$(X_j / X_i)_{\text{cr}} = - L_{ii} / L_{ij}. \qquad (11.5.3)$$

The force relations of such a kind have been called the "superposition effects" of irreversible processes. Thus the possibility of establishing incomplete (mechanical, thermal, chemical, electrical, etc) equilibrium is essentially refused in the systems, for which an external constraint does not allow reaching complete (thermodynamic) equilibrium. As will be seen hereafter, only the refusal to find the forces from the entropy generation expression and changing to their definition as the derivative of system energy (2.3.8) allows returning the usual form $\mathbf{X}_i = - \mathbf{X}_j$ to the equilibrium conditions.

The next paralogism appears when the entropy rise principle is applied to the similarity theory and the productivity of heat engines. The point is that this principle requires the positive definiteness for the matrix of phenomenological coefficients (5.1.9) that the Onsager reciprocal relations to be fulfilled. The associated limitations for the values of the phenomenological coefficients lead to the fact that the maximum efficiency of any flow energy converters can not exceed $\approx 17.5\%$, which does not conform to reality

In the theory of biological evolution the entropy rise principle leads to the fact that when finding the motive forces $\mathbf{X}_i$ of biological processes and the force-associated fluxes $\mathbf{J}_i$ from (5.1.4) the latter always take the

the sign similar to the forces (since $dS/dt = \Sigma_i \mathbf{X}_i \cdot \mathbf{J}_i > 0$). This immediately excludes the possibility for these forces to work against equilibrium and for the self-organization processes to gain a natural explanation, where $\Sigma_i \mathbf{X}_i \cdot \mathbf{J}_i < 0$.

The application of this principle to the evolution theory for isolated systems like the Universe as a whole further complicates the situation. The point is not only in the statement about the "heat" death of the Universe. Any criterion of evolution for heterogeneous systems must take into account their main feature – the opposite direction of any processes running therein (see Chapter 1). Especially this concerns the energy conversion processes in such systems. In order to prove the opposite nature of the processes in such systems, let us express their energy U as the integral $U = \int \rho_u dV$ of the energy density ρ_u. This energy for all internal processes remains constant so that the derivative of energy U with respect to time t is always equal to zero for them:

$$dU/dt = \int (d\rho_u/dt)dV = 0 . \tag{11.5.4}$$

This integral being equal to zero is possible in only two cases: when no processes occur in the system ($d\rho_u/dt = 0$ all over) and when the direction of the processes in different domains of the system is opposite so that the energy density increases in some domains of the Universe and decreases in others. Entropy describing the behavior of the Universe only as a whole can not allow for this main feature of its evolution. Meanwhile, to study these internal processes is the major target of astrophysics.

All the aforementioned evidences that the application of the entropy criteria to solve many problems of natural science is an attempt to do it by knowingly unsuitable means. Hereafter we will make sure that all other paralogisms of thermodynamics are associated with entropy one way or another. The question is how long we shall continue to render "tribute" to our delusions.

Chapter 12

THERMODYNAMIC RESOLUTION OF "GIBBS PARADOX"

Among the paradoxes of physics it can hardly be found one more equally as famous and enigmatic as the "Gibbs' paradox", viz. a statement that entropy builds up stepwise at changing from identical gases to a

mixture of gases arbitrarily little distinguishable in their macro-physical and micro-physical properties (J. Gibbs, 1950). For a century this fact has not once become the object of investigation for both physicists and philosophers. To many of its investigators it seemed they could eventually explain why the entropy jumped with so queer independence from the degree and character of distingushability between the gases mixed, as well as why the notion "entropy of mixture" was inapplicable to identical gases. However, like the legendary sphinx that paradox has been thrashed over on pages of scientific books and magazines and has not yet left them till nowadays. As a result, the majority of its investigators have inclined to an opinion that the "Gibbs paradox is unsolvable on the plane of classic thermodynamics (B. Kedrov, 1969).

Other vistas open up to this problem from the positions of energodynamics. This chapter is dedicated to show that the Gibbs paradox is actually paralogism, viz. an erroneous statement sounding credible due to the statistic-mechanical interpretation of entropy as a measure of "any and all" irreversibility. As an alternative, the thermodynamic theory of irreversible mixing processes will be offered as allowing for the dependence of losses from the nature of gases being mixed.

12.1. Origin and Nature of «Gibbs' Paradox»

In his famous work "On Equilibrium of Heterogeneous Substances" (1875–1876) J. Gibbs set forth the following expression for the entropy of an ideal gas mixture:

$$S = \Sigma_k N_k(c_{vk}\ln T + R_k\ln \upsilon_k + s_{ok}), \qquad (12.1.1)$$

where R_μ – universal gas constant; N_k – mole number of the kth substance; c_{vk}, υ_k, s_{ok} – isochoric heat capacity, partial volume and entropic constant of a mole of the kth substance, respectively [1].

Gibbs wrote this expression by analogy with Dalton law to which the pressure of an ideal gas mixture p is equal to the sum of partial pressures of the components p_k ($p = \Sigma_k p_k$). When postulating this "similar principle regarding the gas mixture entropy", Gibbs made no mention whatever of what the individual characteristics s_{ok} and c_{vk} meant having them evidently assumed identical properties of a corresponding pure substance.

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[1] Here, unlike the original, 1 mole is adopted as a quantity unit of the kth substance

It is significant that Gibbs did not at all consider expression (12.1.1) as rigorously proven. He just assumed it would have been correct to initially accept this relationship as a fundamental equation describing an ideal gas mixture and then to substantiate the validity of such definition by properties which might have been derived from it. Applying this expression to the diffusion at the mixing of ideal gases as two separate masses, each of the gases initially occupying half a complete volume, he defines that the difference between the gas mixture entropy $S = (M_1R_1\ln V + M_2R_2\ln V)$ and the entropies before mixing constitutes the constant value

$$S - [M_1R_1\ln(V/2) + M_2R_2\ln(V/2)] = R_s \ln 2, \qquad (12.1.2)$$

where $R_s = M_1R_1 + M_2R_2$ – universal gas constant of the system as a whole.

Commenting on this result Gibbs notes, "It is significant that the value of this expression does not depend on kinds of the gases being mixed and degree of their difference"… since the "value pV/T is entirely defined by the number of molecules being mixed". Thus Gibbs himself traced nothing paradoxical in that result. However as investigators were studying the question, they encountered ever growing difficulties, which caused the "Gibbs' paradox" definition.

In voluminous literature dedicated to this question several standpoints are met regarding the nature of this paradox. A number of investigators (M. Leontovich, 1951; A. Samoilovich, 1955; P. Chambadal, 1963; S. Fraier, 1973, and others) identify the nature of the paradox with the impossibility of a limit change to identical gases in expression (12.1.1). In fact, (12.1.1) does not contain any parameters describing the difference between gases. Therefore it necessarily follows from this expression that entropy jumps when portions of the same gas are mixing. Gibbs himself having adhered to the Boltzmann's (probabilistic) interpretation of entropy saw nothing queer in that since a "mixture of the same-kind gas masses in principle differs from that of the different-kind gas masses" – for lack of information allowing, in principle at least, to separate them. However such an argument is evidently unacceptable from the positions of thermodynamics wherein the initial information of a system is restricted to definition of the thermal and caloric equations of state identical for ideal gases.

Some investigators refer to the Gibbs' theorem itself as a paradox. According to it, the entropy of a gas mixture is equal to the summary entropy of particular gases, each occupying the volume of the whole mixture at the same temperature. Gibbs substantiated this statement by an imaginary experiment on the reversible separation of gas mixtures thru

semipermeable membranes. However an imaginary experiment may be used in thermodynamics to substantiate some statement providing its conclusions do not contradict theory only (K. Putilov, 1974). Therefore many investigators have not taken this "proof" as convincing. Herein multiple attempts are rooted to more rigorously prove the entropy additivity in the Gibbs' concept. The proofs of the said theorem insomuch offered are reduced to two main categories:

a) Method of semipermeable membranes, which, besides Gibbs himself, was used by Rauleich, 1875; L. Boltzmann ,1878; A. Wiedeburg, 1894; A. Bik,1903; B. Tamman, 1924; V. Nernst, 1929; P. Chambadal, 1963; B. Kedrov, 1969, and others.

b) Method of gas column in gravitational field, which, in particular, H. Lorenz (1927) and E. Schrödinger (1946) used.

All these methods were aimed to define the work of reversible mixture separation and eventually based, explicitly or implicitly, on the assumption of ideal membranes capable to provide the so-called "membrane equilibrium" (when the gas mixture pressure on one side of the membrane is counterbalanced by the partial pressure of one of the components on its other side). It is significant that in all imaginary experiments of such a kind after-investigators discovered a number of inaccuracies and disputable assumptions. Furthermore, from such reasoning based on "asymmetrical" semipermeable membranes (letting gas through in only one direction) results were obtained antipodal to the Gibbs' theorem (P. Chambadal, 1963). Those proved the additivity of component entropies found at the total pressure and temperature of the mixture when no entropy jump appeared at all.

A number of investigators (V. Luboshits, M. Podgoretsky, L. Gelfer, 1971, 1975; E. Gevorkian, R. Gevorkian, 1975, 1976) adopt a neutral attitude toward the Gibbs' paradox considering the entropy jump as quite natural for gases modifying their properties discretely. In this case it is unclear how far different (from a thermodynamic standpoint) such substances are as: isotopes (different in molecular mass, but equal in chemical properties), isobars (different in chemical properties, but equal in molecular mass), isomers (different only in their life span in excited state), optical antipodes (different optically due to different spatial grouping of molecules), etc.

Depending on investigators' attitude toward the Gibbs' paradox their interpretation of its "solution" varies. The overwhelming majority of investigators accept the statement of the mixing process entropy existing as a true one though sounding somewhat unusual and incredible. These investigators after Gibbs refer the entropy jump at the mixing to (1) principal impossibility of after-separation of the same-kind-gas mixture; (2) principle difference of physical and chemical properties of gases regard-

ing the character of their variation (M. Planck, 1925); (3) discrete varia-
tion of atomic properties (E. Schrödinger, 1946; R. Kubo, 1970; A.
Samoilovich, 1955; A. Sommerfeld, 1955; L. Terletsky, 1966; I. Bazarov,
1976); (3) density discontinuity at the mixing of various gases (P.
Lelouchier, 1975); (4) some work to be done to create partial pressures
(B. Kedrov, 1969), etc. Other investigators see the solution to the Gibbs'
paradox in proving the fact the mixing process entropy depends on the
degree the gases differ from each other (V. Luboshits, M. Podgoretsky,
1971; Y. Varshavsky, A. Sheinin, 1968; R. Gevorkian, E. Gevorkian,
1976), e.g., for a mixture of the same gases with a continuously equaliz-
ing composition.

It is just a minor part of investigators (J. Van der Vaals, F. Kon-
stamm, 1911; P. Postma, 1927; P. Chambadal, 1963; A. Veinik, 1967; B.
Casper, S. Fraier, 1973; M. Biot, 1977) including the author of this book
(V. Etkin, 1973, 1991), who deny any entropy variations at the mixing of
non-interacting gases, which is the most radical solution to the said para-
dox.

12.2. Thermodynamic Inadmissibility of the Gibbs' Paradox

There are a number of arguments evidencing that the Gibbs' paradox
is actually paralogism, viz. an erroneous statement sounding credible in
the conviction that entropy rises in any irreversible process. It is impossi-
ble to reproduce herein all arguments of various authors to substantiate
this thesis. Therefore we will not go beyond those of the arguments
which are of the methodological character and therefore sound most con-
vincing.

Classic thermodynamics dealing with only closed systems is known
to have been interested in only the variation of entropy, but not its magni-
tude. This entropy variation in course of some process does not depend
on whether a system is considered as a mixture of the kth ideal gases or as
a set of the same ideal gases separated with a movable heat-permeable
membrane since from the thermodynamic standpoint all properties of a
system are defined by exclusively its thermal and caloric state equations.
This entropy variation for a system with an arbitrary and constant (in
whole) composition is derived from a known expression:

$$\Delta S = \Sigma_k N_k R_\mu \ln T/T_o - \Sigma_k N_k R_\mu \ln p/p_o, \qquad (12.2.1)$$

where T_o, p_o and T, p – absolute temperature and pressure of the gas mix-
ture at the beginning and at the end of whatever process, respectively.

It follows from the identity of equations (12.2.1) for a gas mixture or a set of pure gases that from the positions of thermostatics they have the same number of degrees of freedom. This number is defined by the number of independent variables of state and is equal to 2 for gases (thermal and mechanical degrees of freedom). Hence the thermodynamic properties of a system under consideration (either a gas mixture or a set of pure gases) are to the full extent characterized by two (thermal and caloric) state equations in the form:

$$pV = MRT;\ U = C_vT, \tag{12.2.2}$$

where $R,\ C_v = \Sigma_k N_k c_{vk}$ – universal gas constant and total isochoric heat capacity of the system, respectively, found experimentally without knowing its composition and studying properties of its components separately. At these conditions the definition of any other properties of the system, e.g. its composition, is superfluous. Gibbs himself admitted this fact having noted that for a constant-composition system the "state is completely characterized by the total mass M so that the knowledge of the composition of a system is not the necessary condition to derive its state equations". Hence both the gas mixture entropy and the gas set entropy as functions of system state were defined by two parameters of system state ($T,\ p$ or $T,\ V$) and due to their constancy at isobaric-isothermal mixing remained unvaried. Thus from a thermostatic standpoint none process ran, the more so because none of energy effects were observed at that. In fact, the aggregate system with two degrees of freedom yet before mixing was in total (both thermal and mechanical) equilibrium. Gibbs quite realized that when noted that the "problems of thermodynamics refer just to the system states defined by such incomplete way". Therefore the Van der Vaals' standpoint (1911) is quite reasoned when he noted regarding the mixture of isotopes, "However, from a thermostatic standpoint the mixture of such substances should be considered as a single substance and, since entropy is defined as thermostatic, there are no reasons to talk of an entropy rise at diffusion".

Another contradiction is revealed in the thermodynamic approach to the problem of entropy constants' additivity at the mixing. In fact, Gibbs' equation (12.1.1) was based on the analogy of the fundamental equation with Dalton law

$$p = \Sigma_k M_k R_\mu T/V \tag{12.2.3}$$

With regard to equation (12.1.1) Gibbs notes that this expresses a known principle, according to which the pressure of a gas mixture is equal to the sums of the pressures the components of this gas mixture

would have providing they exist separately at the same volume and temperature. Thus Gibbs was explicitly based on additivity of entropy for each of the components as expressed by the relationship $S = \Sigma_k N_k s_k$.

Let us clarify now whether expression (12.1.1) complies with this relationship if the value s_{ok} assumed constant in processes of system composition variations. The additivity (summability) of whatever extensive parameter is known to suppose its specific value does not depend on mass. In other words, additive values are homogeneous mass functions, i.e. comply with Euler's theorem which in entropy application has the form:

$$\partial S_k(N_k)/\partial N_k = S_k(N_k)/N_k .\qquad(12.2.4)$$

Expression (10.2.4) is compatible with (10.1.1) when the derivative $(\partial S_k/\partial N_k)$ does not depend on N_k. However, it is easy to see that at $s_{ok} = $ const the entropy S_k of a particular component does not meet this requirement. It really follows from (12.1.1):

$$\partial S_k(N_k)/\partial N_k = s_k(N_k) - R_\mu,\qquad(12.2.5)$$

i.e. is a function of N_k. Hence the Gibbs' assumption that $s_{ok} = $ constant and the same before and after mixing is groundless.

One more contradiction revealed by B. Kedrov (1969) is that the variation of ideal gas mixture entropy depends on the process path. Let a vessel A contain a mixture of two moles H_2 (hydrogen) and two moles Cl_2 (chlorine). The vessel is kept in darkness so that a chemical reaction within it is practically "inhibited". Let us separate the mixture with a partition into two equal parts and initiate in one of them by exposure to light an isobaric-isothermal chemical reaction resulting in generating two HCl molecules. As a result of the chemical reaction, the entropy of this part of the system will vary by some value ΔS_x. Let us now remove the partition between the first half of a system containing the H_2+Cl_2 mixture and the second half containing the HCl gas. Owing to the fact that the gases are different in both halves of the vessel, according to the Gibbs' mixing theory the system entropy will rise by some value ΔS_{mix}. Now let us expose the both halves of the vessel to light – the reaction will develop further with one more HCl mole generated and the entropy further varied by ΔS_x. The total entropy variation in the three said processes resulted in two HCl moles generated is equal to $2\Delta S_x + \Delta S_{mix}$. However, the same two HCl moles could be obtained by exposing the mixture to light as a whole, i.e. without its separation followed by mixing. In this case the gas mixture entropy would evidently vary by only a value of $2\Delta S_x$. Since the initial

and final state of the system and the heat effect of the reaction are the same in both variants, a contradiction is present.

Further contradiction is revealed when using the mixing process entropy to calculate the exergy (capability for technical work) losses of the systems workability at the mixing of gases. According to the Gibbs' mixing theory which does not involve any parameters characterizing differences between gases, the workability loss $-\Delta E_{mix}$ at the mixing of substances featuring ideal gas state (i.e. complying with the Clapeyron equation) is defined by exclusively the mixing process entropy ΔS_{mix} and the environmental temperature T_0 and does not depend on the chemical nature of the substances being mixed:

$$- \Delta E_{\mathrm{mix}} = T_{\mathrm{o}} \Delta S_{\text{см}}. \qquad (12.2.6)$$

Let us consider, however, a fuel cell, to which electrodes, e.g., oxygen and hydrogen are fed separately under a minor pressure (so that their state would not differ from ideal gas). The chemical affinity in reversible fuel cells is known to be realized in the form of electric current work which is theoretically equal to the chemical affinity value. Now let us mix oxygen and hydrogen partly or completely before feeding them to the fuel cell electrodes, i.e. let us feed not pure gases, but some oxy-hydrogen mixture. The similar experiments have repeatedly been conducted and are known to have led to drop of the voltage developed by the fuel cell down to total disappearance of current in the external circuit. Hence the actual loss of fuel cell capability for work depends on the nature of gases being mixed (their chemical affinity) and reaches the 100% value when the reaction becomes thermodynamically irreversible. This example is even more remarkable because allows to distinguish the losses at the mixing and chemical transformation. From this example it follows that the major losses arise not during mixing of gases, but in subsequent chemical reaction which due to this becomes thermodynamically irreversible. Therefore it would be more correct to refer in this case not to losses at the mixing, but rather losses due to mixing.

Inapplicability of the Gibbs-obtained result shows up when as well estimating the capability for work of whatever substance which concentration differs from its environmental concentration[1]. Classic thermodynamics according to the Gibbs' theory gives the following equation for the exergy of working medium in flow Ex_p (Szargut J., Petela R.,1968):

$$Ex_{\mathrm{p}} = H - H_{\mathrm{o}} - T_{\mathrm{o}}(S - S_{\mathrm{o}}) + R_{\mathrm{c}} T_{\mathrm{o}} \Sigma_k \ln p_k / p_{ok}, \qquad (12.2.7)$$

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[1] This allows in-principle constructing an engine using this concentration difference

where H, H_o и S, S_o – enthalpy and entropy of a working medium (gas) at initial state and at equilibrium with the environment, respectively; p_k, p_{ok} – partial pressures of the ith substance in initial mixture and in the environment, respectively.

The last term of this expression defines the so-called "chemical" (more exactly, concentration) exergy caused by the difference between partial pressures of the kth substances in the system p_k and the environment p_{ok}. This may supposedly be realized with the help of semipermeable membranes which allow isothermally expanding the gas from the pressure p_k to p_{ok} in an expanding machine with heat obtained from the environment and useful external work done.

As follows from this expression, the unit mass exergy for an ideal gas does not depend on its chemical nature and tends to infinity as its environmental concentration is decreasing. Inapplicability of such a conclusion is evident.

Thus estimating the Gibbs' approach to the gas mixing theory it has to be admitted that this gives no answer to not only the most important question about criteria of difference or identity of gases being mixed, but either about the theoretical value of work to be done to separate the mixture. The experiment shows that the less the difference between the mix components, the more the work on gas separation, even to say nothing of the test hardware imperfection. In particular, when producing nuclear fuel by separating a gas mixture containing 99,3% $U^{238}F_6$ and 0,7% $U^{235}F_6$, it is theoretically required (allowing for mixing process entropy) 0.023kWh of energy per 1kg of the second component. However, the actual energy consumption amounts to $1.2 \cdot 10^6$ kWh, i.e. approximately fifty million times as much (J. Ackeret, 1959). Thus the Gibbs' mixing process entropy can not serve as a basis for even approximate estimation of the theoretical mix separation work.

12.3. Entropy Reference Point Shift in Mixing Process as Entropy "Jump" Reason

Far from all investigators of the Gibbs' paradox have related this with the change to investigation of open system in the Gibbs' concept. In fact, considering the ideal gas mixture entropy or ideal gas set entropy from the positions of "pre-Gibbs" thermodynamics of closed systems as a composition function, i.e. $S = S(T, p, N_k)$, the entropy at the mixing will remain unvaried since the temperature, pressure and mole numbers N_k (masses M_k) of all system components remain unvaried at that. In other words, for the diffusion process in its intrinsic meaning as the concentra-

tion equalization in a closed system the entropy remains unvaried despite the irreversibility of this process.

Let us consider now the isobaric-isothermal mixing process in the Gibbs' concept as a composition variation in each of the open subsystems due to the exchange of the kth substances among them (i.e. a mass transfer among them). In this case, because additional degrees of freedom appear (related to the kth substances exchange), the exact differential of the system entropy becomes:

$$dS = (\partial S/\partial T)dT + (\partial S/\partial p)dp + \Sigma_k (\partial S/\partial N_k)dN_k . \qquad (12.3.1)$$

The first and the second partial derivatives in this expression are defined at constant composition and mass of the whole system (M_k = const, $\Sigma_k M_k$ = const) and may be found from the joint equation of the 1st and the 2nd laws of thermodynamics for closed systems. In particular, for the derivative of entropy with respect to temperature from (12.1.1) via caloric state equation (12.2.2) the following forms may be found:

$$(\partial S/\partial T)_{V,N} = C_v/T ; (\partial S/\partial P)_{T,N} = - MR_c/P. \qquad (12.3.2)$$

As for the derivative $(\partial S/\partial N_k)_{T,V}$, this can not be defined only based on the laws of thermodynamics for closed systems. To define this, relationship (12.1.1) should be applied, which gives:

$$(\partial S/\partial N_k)_{T,V} = s_k , \qquad (12.3.3)$$

where s_k – partial molar entropy of the kth component, i.e. the value characterizing the entropy S rise in an open system when one mole of the kth substance enters in it at isobaric-isothermal conditions, whereas the mole number of other, j^{th} substances, does not vary ($k \neq j$).

Thus for open systems the exact differential of the entropy $S = S(T,p,N_k)$ is:

$$dS = (C_v/T)dT + (MR/V)dV + \Sigma_k s_k dN_k. \qquad (12.3.4)$$

Integrating this expression from an initial arbitrary state with the entropy S_0 assuming C_v constant and allowing for the relationship $dV/V = d\upsilon/\upsilon$ evident at N = const gives:

$$S = C_v \ln T + NR_\mu \ln \upsilon + \Sigma_k \int s_k dN_k + S_o . \qquad (12.3.5)$$

This expression differs from (12.1.1) offered by Gibbs by the third term appeared on the right-hand side and describing the entropy variation at gas mixing. This is what Gibbs neglected when having integrated equation (12.3.4) with respect to only the variables T and V. As a result, he defined the entropy to an accuracy of some function of state $S_o(N_k)$, i.e. obtained not the entropy constant, but some function of composition as the sum of the two last terms on the right-hand side of expression (12.3.5). This value necessarily varies at the mixing in course of diffusion of the kth gases.

It may be easily shown that at the mixing to the Gibbs' concept both the mix entropy and its reference point, i.e. the $S_o(N_k)$ value, vary simultaneously and equally.

Let us consider the same gas set system which Kedrov used in his imaginary experiment when mixing H_2 and Cl_2. Let us assume after Gibbs that $s_{ok} = 0$, $S_o = 0$. Let us further transfer the system via an arbitrary quasi-static (e.g. isochoric) process to a state with a temperature of T_1 and volume V_1. The entropy of the system will then rise by a value $\Delta S_{0-1} = \Sigma_k N_k R_\mu \ln T_1/T_o$. Now let us remove the partition and provide the isobaric-isothermal mixing where the system volume remains unvaried ($V_1 = V_2$), whereas the entropy according to the Gibbs' theory rises by some value ΔS_{mix} and becomes equal to $S_2 = S_1 + \Delta S_{mix}$. Then let us cool the mixture obtained down to a state with a temperature of $T_3 = T_0$. The entropy will subsequently decrease by a value of $\Delta S_{2-3} = -\Delta S_{0-1}$. The system has again returned to the state with the same temperature and volume, however, now the entropy in this state (which we adopt as initial) is equal to $S_3 = S_2 + \Delta S_{2-3} = S_o + \Delta S_{mix}$. Thus the gas mixture entropy value at the reference point parameters has varied by the exact mixing process entropy value! In other words, *in a diffusion process as the subject of the Gibbs' concept not the entropy itself experiences a jump, but its reference point!* Other result could hardly be expected since the Gibbs' mixing process entropy does not depend on temperature and hence is the same both in its current state and an arbitrary reference point. As a matter of fact, applying expression (12.1.1) to an arbitrary reference point for entropy any unbiased investigator would arrive at a conclusion that this reference point has as well experienced the same jump. Thus the entropy jump, should it really take place, equally relates to also the entropy reference point since this jump depends on only the ratio of mixed gas volumes before and after mixing. However, to justify the fallacy, it should be noted that in the days of Gibbs the problem of the entropy reference point selection and the entropy magnitude definition, which has eventually led to the third law of thermodynamics, did not yet exist. This is the circumstance that, in our view, engendered the Gibbs' paradox. It should seem so that the after-investigators could not have omitted the fact. They knew

the third law of thermodynamics. It is this law that defines the reference point for entropy of all condensed substances. As a matter of fact, according to the third law of thermodynamics "as temperature is approaching the absolute zero, the entropy of any equilibrium system in isothermal processes ceases depending on whatever thermodynamic state parameters and to the limit $T = 0$ adopts a constant value, the same for all systems, which may be assumed as zero" (I. Bazarov, 1976). Therefore such a shift of the entropy reference point comes into antagonism with the third law of thermodynamics which reads that the entropy of whatever equilibrium system at the absolute zero temperature adopts a constant value, the same for all systems, which may be assumed as zero. Thus the entropy reference point jump as ensuing from the mixing process to the Gibbs' concept leads to a conflict with the third law of thermodynamics. This fact, which is, as far we know, beyond other investigators' comments, exactly reveals the paralogism of the Gibbs' paradox.

From the above-mentioned it becomes clear why some of the investigators, based on imaginary experiments, came to the necessity of calculating the mixture entropy from the mixture total volume, whereas the others – from the total pressure and temperature of the mixture. The fact is that both of these standpoints are equally valid and applicable since neither of them leads to a jump of entropy at the mixing of non-interacting gases.

Hence from the positions of energodynamics as well the Gibb's conclusion of a step rise of entropy at the mixing of ideal gases appears as an erroneous statement caused by the arbitrariness in choosing the reference point of entropy for open systems, i.e. by the violation of the third law of thermodynamics. This result shows that in thermodynamics the Gibbs' paradox does not take place whatever meaning is read into it. As for statistic and informational entropies, the jump is not something paradoxical here since the number of possible permutation of particles depends on whether the gases are considered identical or distinguishable.

12.4. Thermodynamic Theory of Mixing Processes

The gas mixing theory must give a solution to two problems, viz. the definition of the useful (free) energy of a particular mixture and the work needed for its separation. The answer the Gibbs' theory gives solves neither of them. This is a challenge to approach the issue from the positions of energodynamics. Energodynamics considers the mixing as an irreversible process of equalizing the concentrations of the components all over the system volume while keeping their number unvaried for the sys-

tem as a whole. This corresponds to the strict import of the word "diffusion" (from the Latin "diffusio" meaning spreading). Such a redistribution of components involves the variation of the moment of the kth substances' distribution $\mathbf{Z}_k$. As any irreversible process, this may be maintained from outside, e.g. by feeding the kth substances across the system borders. However, this is independent of the transfer of these substances across the system borders (diffusion across the borders), i.e. of the diffusion to the Gibbs' concept. The latter, for the avoidance of mishmash, we have named above the *selective mass transfer* of a system. The considered process involves a variation of the mass of the whole system $M = \Sigma_k M_k$ or the mole number in it $N = \Sigma_k N_k$. Unlike this, the diffusion leaves M and N unvaried. In fact, the mixture component distribution may be equalized also in the absence of a substance transfer across the system borders as it occurs, e.g. under the influence of electric or centrifugal fields. Thus the mixing is a specific qualitatively distinguishable irreversible process irreducible to other processes. This can not be approached by the "adaptation" to whatever other process.

The diffusion coordinate for the kth independent substance is the moment of its distribution $\mathbf{Z}_k$, while the motive force $\mathbf{X}_k$ – the component potential concentration gradient which is defined by the uniqueness conditions of the mixing process and, according to paragraph 10.5, above means the negative gradient of diffusive, osmotic, etc. potential. The diffusion process is irreversible and involves thermal and bulk effects resulting in internal sources of entropy and volume appeared. To find these sources, let us represent the entropy S and the mixture volume V in terms of their partial molar values s_k and υ_k, respectively:

$$S = \Sigma_k N_k s_k; \; V = \Sigma_k N_k \upsilon_k , \qquad (12.4.1)$$

and considering (10.5.6) obtain:

$$\Delta S_{mix} = \Sigma_k N_k (s_k - s_{ko}); \; \Delta V_{mix} = \Sigma_k N_k (\upsilon_k - \upsilon_{ko}). \qquad (12.4.2)$$

The value $(s_k - s_{ko})$ in this equation characterizes the variation of entropy of the kth pure substance s_{ko} in the mixing process, while the associated heat

$$q_k^* = T(s_k - s_{ko}) \qquad (12.4.3)$$

– thermal effects arising at the mixing of interacting components[1]. These effects are caused by the available partial molar entropy (defined by an actual increment in mixture entropy s_k at isobaric-isothermal input of the unit k^{th} substance) and by the entropy s_{ko} superinduced from outside by one mole of the pure k^{th} substance. This means that the above value belongs to the thermodynamic function of mixing. Similarly the difference $\Sigma_k N_k(v_k - v_{ko})$ characterizes the bulk effects arising at the mixing of interacting components, while the value

$$w_k^* = p(v_k - v_{ko}) \qquad (12.4.4)$$

– cubic strain work involved in these effects. For non-interacting substances the thermal and the bulk effects ($s_k - s_{ko}$; $v_k - v_{ko}$) at input of the kth substance are absent ($q_k^* = w_k^* = 0$), which confirms the above conclusion that the ideal gas mixing process entropy is absent.

Thus the thermal and the bulk effects q_k^* and w_k^* described by expressions (12.4.3) and (12.4.4) may serve as a measure of mixing process irreversibility. These relationships allow answering all questions raised above in the thermodynamic mixing theory. According to them the theoretical work on mixture separation depends on the nature of gases being separated and for non-interacting gases becomes zero along with the difference $s_k - s_{ko}$. This circumstance leads to a necessity to distinguish the vector and the scalar stages of an energy dissipation process. Let us elucidate this by example of a fuel cell realizing the chemical affinity of reagents in the form of electric work. If the reagents, before fed to the fuel cell electrodes, are allowed to be completely mixed, the fuel cell emf is known to fall down to zero. The mixing process has the vector nature according to the tensor order of its coordinates $\mathbf{Z}_k$. Though this stage is irreversible and involves thermal and bulk mixing effect, it just a little changes the value of reagents' chemical affinity. However, this stage results in that the subsequent homogeneous chemical reaction becomes thermodynamically irreversible with the charges not separated and useful work done, but with a heat released in amount equivalent to this work. Thus the capability for work is lost as a result of the spatial homogeneity spontaneously set in for the chemically reacting system, but not the subsequent chemical reaction itself. The chemical energy appeared to have already been dissipated by the beginning of this reaction and there was

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[1] In the theory of irreversible processes (TIP) the value q_k^* is introduced as one of the transport factors L_{kj}, while its interpretation as the energy transported by one mole of the kth substance in the absence of temperature gradient becomes possible just "a posteriori" (by experimental results)

nothing for it but to pass into the random energy (heat). In other words, the chemical energy of the reacting mixture appeared to have already been less ordered than the initial energy of the spatially separated re-agents. It is referred to the fact that instead of a macro-heterogeneous system we have got the micro-heterogeneous one differing in just the structure (configuration) of the molecules and atoms comprising it. However, this is not yet the heat energy of reaction products! Thus we come to a necessity to distinguish between the macro-physical stage of a dissipation process involving the disappearance of system spatial heterogeneity (it is expressed mathematically by "scalarization" of the process, i.e. loosing its vector nature) and its micro-physical stage associated with scaling heterogeneity down to a mere random form of energy obtained. Using equation of displacement vectors' balance (2.6.2) the first stage may feature the value

$$W^d = \Sigma_i \mathbf{F}_i \cdot d_s \mathbf{r}_j, \qquad (12.4.5)$$

which may be named the "dissipation micro-work".

The second, micro-physical, stage of the dissipation process reflects the destruction of a chemically reacting system. This stage as well involves the internal "disggregation work" (R. Clausius) done. However, this work features already the scalar character and must be described as the "dissipation micro-work". This is the work that defines the decline of free energy of a chemically reacting mixture. In a general case this category of work should include not only the scalar chemical reaction work, but as well any work associated with further "disordering" of the substance (rearrangement of its molecular, crystal, cluster, etc. structure).

Hence the standard affinity of a homogeneous chemical reaction is partly consumed to prepare the reaction mixture (vector stage of the process not obeying the stoichiometric proportions), and then – to run the reaction itself (V. Etkin, 1991). This may be the reason why the standard affinity of a reaction can not play the part of its thermodynamic force (G. Gladyshev, 1991). Anyway, the possibility to distinguish between the thermal effects of mixing and subsequent chemical reaction may serve as the incentive to further investigations.

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Chapter 13

UNFOUNDEDNESS OF CONCTPTION OF NEGATIVE ABSOLUTE TEMPERATURES

The concept of negative spin temperature was originally introduced into theoretical physics as some elegant notion that allowed "laying a bridge" in-between nuclear magnetism and thermodynamics. Expediency of such a notion was estimated thru the experimental data interpretability. However, it was soon discovered that such an extrapolation of the thermodynamic notions and methods led to a conflict with the law of excluded perpetual motion of the second kind and to a necessity of its "inversion". This chapter aims at demonstrating the fallacy of such notions and outlining ways of eliminating the methodological errors that have led to those.

13.1. Non thermodynamic Nature of Negative Absolute Temperature

The notion of negative absolute temperature was introduced in the late XX century after subsystems had been discovered, wherein thru the magnetic field inversion or high-frequency pulse the energy-level "population inversion" had been successfully created. This is construed as a state wherein the prevailing number of energy carriers (nuclear spins, in this case) are, unlike the usual state, on a higher energy level (I. Bazarov, 1976). Some of these subsystems are rather self-sufficient in the effect that the "particles" constituting the system of nuclear spins quite quickly come to equilibrium between themselves and, on the contrary, slowly enough – with the remainder part of the system (crystal lattice). Investigations have shown that the subsystems of such kind may be distinguished in the composition of many bodies, in particular, in a number of crystals. Such is, e.g., the nuclear magnet system of lithium ions in the lithium fluoride crystals (LiF).

The notion of temperature was then applied to describe the population-inversion spin systems wherein temperature had to be endued with negative value. The reason for that was as well the said statistical interpretation of entropy and absolute temperature. If the statistical state probability is accepted identical to the thermodynamic entropy on the ground that both these values are additive and reach a maximum in the equilibrium state (Boltzmann law), then comparing the derivative $(\partial U_s / \partial S_s)$ for

the statistically defined internal energy U_s and the entropy S_s with the well-known definition of the thermodynamic temperature

$$T \equiv (\partial U/\partial S)_V, \qquad\qquad (13.1.1)$$

gives that the distribution parameter β in the Boltzmann equation for the population n_i of some i^{th} energy level ε_i

$$N_i = N_0 \exp(-\beta \varepsilon_i) \qquad\qquad (13.1.2)$$

is related with the absolute temperature T by a simple relationship $\beta = 1/k_b T$, где k_b – Boltzmann constant. From this it follows that the population n_o of the "zero" energy level ε_o relates to the population N_i of the ith energy level ε_i as

$$N_i/N_0 = \exp[(\varepsilon_0 - \varepsilon_i)/k_b T]. \qquad\qquad (13.1.3)$$

If $T > 0$, then the population of higher energy levels according to (13.1.3) decreases by exponential curve. However, if an equilibrium state with the population inversion is obtained, when the majority of particles are on the upper energy level, this state should be endued with negative absolute temperature T<0 statistically defined. Thus from the statistical-mechanical positions the application of the concept of temperature (both positive and negative) to spin subsystems sounds not less reasonable than, say, the notion of electron temperature in plasma or magnetic temperature in magnetic materials (N. Ramsey, 1956).

It should be noted that the existence of systems with the population inversion is now a fixed fact. The population inversion in such installation as lasers is created by "uploading" them with the microwave radiation generating a stationary non-equilibrium state of the system. However, the population inversion is not yet enough to operate with negative absolute temperature. It is important the system to be in equilibrium at the population inversion. This needs, firstly, the particles constituting the subsystem to attain internal equilibrium between themselves much sooner than with the environment or the remainder part of the system. Secondly, the energy spectrum of such subsystems must be restricted from above so that attaining the population inversion would not demand infinite energy to be supplied. The first subsystem meeting these requirements was the above-mentioned nuclear spin system of lithium ions in the lithium fluoride crystals (LiF). If the LiF crystals are placed in the magnetic field, the nuclear magnets can in principle occupy four different energy levels including those in the field direction (lower energy level), across the field

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and anti-parallel the field (upper energy level). Should now the external field direction be quickly changed (as it was in the experiments made by E. Pursel and R. Pound, 1951), the nuclear magnets will not be able to follow this, and the major part of them will appear in the upper energy level, i.e. the population inversion will occur. After minor and quickly collapsing oscillations the nuclear magnets will come to mutual equilibrium. This will occur for a time t_2 much inferior to the time t_1 of attaining equilibrium between the spin subsystem and LiF crystal lattice (5 thru 30 minutes), which allows concluding of a certain "self-sufficiency" in the spin subsystem behavior.

It was also experimentally found (E. Pursel and R. Pound, 1951) that if the LiF crystal was withdrawn from a magnetic field and placed in the weak geomagnetic field and then in several seconds returned to that initial, its final magnetization would appear not much lower than the initial one. E. Pursel and R. Pound repeated the same experiment with a subsystem which initial magnetization was opposite to the field. In this case, after the specimen had been placed in the geomagnetic field and then returned to the strong magnetic field, not only its magnetization value was recovered, but also the magnetization orientation opposite to the field. The most amusing here was the fact that the specimen having been in a field much weaker that the local field of the test stand did not lead to the magnetization totally destroyed. The last circumstance substantiated the two men's conclusion of two types of interaction having existed: a spin-spin interaction that led to an internal equilibrium quickly reached in the system of nuclear magnets, and a spin-lattice interaction of an unknown nature. The latter was likened to heat exchange. The crystal lattice was taken there to be a thermostat, while the spin system demagnetization – its cooling. With such an interpretation one had to accept that the states with a negative absolute temperature extended the thermodynamic temperature scale beyond the zone of $T = \infty$ and (what is much more important!) to draw a conclusion regarding an "inversion" of the law of excluded perpetual motion of the second kind in such systems (N. Ramsey, 1956).

13.2. "Inversion" of the Second Law in Negative Absolute Temperature Range

The said "inversion" means the possibility of complete conversion of heat into work in such systems and, on the contrary, the impossibility of complete conversion of work into heat (M. Zemansky, 1968; I. Bazarov, 1991). As a matter of fact, let us imagine the Carnot cycle realized at the temperatures of hot and cold bodies T_h and T_c, respectively, less than ab-

solute zero. The thermal efficiency of the reverse Carnot engine will then have the form:

$$\eta_t^K = 1 - Q_c/Q_h = 1 - T_c/T_h. \qquad (13.2.1)$$

By Ramsey, a body is considered as hot in the range of $T < 0$ providing its temperature is higher (i.e. negative temperature modulus is lower). At that $T_c/T_h > 1$, i.e. the thermal efficiency will be negative, while the modulus $|Q_c| > |Q_h|$. This surprising result, by Ramsey's correct remark, means that the Carnot cycle work done within this temperature range will be positive providing heat Q_c is taken from the "cold" body (well), whereas the hotter body is a heat receiver (sink). In this case the cycle will as well run clockwise (since $dS = đQ_c/T_c < 0$ at $T_c < 0$). According to the law of conservation of energy to do positive work, the heat amount $|Q_c|$ must exceed $|Q_h|$. Since thru a heat contact between the well and the sink the entire heat Q_h given to the "hot" body may be returned thru heat transfer to the "cold" body, the work will be done in this continuous cycle sequence due to the heat of the solely "cold" body without any residual changes in other bodies. Along with this Ramsey also drew a conclusion that heat could not completely convert into work. Thus all main provisions of the law of excluded perpetual motion of the second kind suffered "inversion". The most amazing thing is that the conclusion of the second law violation was drawn…from the same second law proper! The fact that heat can completely convert into work actually means that expression (13.1.4) is inapplicable in the range of $T < 0$. In this case, however, all conclusions based on this expression become invalid as well. Despite this "vicious circle" the statement confirming the "inversion" of law of excluded perpetual motion of the second kind has got into educational books (M. Vukalovich, I. Novikov, 1968) and is being reproduced even in the best of them (I. Bazarov, 1991). The latter, e.g., writes, "Perpetual motion of the second kind, i.e. the device that would completely convert heat of whatever body into work (without partial heat transfer to other bodies), is impossible; this statement excluding the inversion for usual systems with $T > 0$ and admitting the inversion for unusual systems with $T < 0$". This fact promotes critical attitude toward the experimental data interpretation and its compliance with the methodological principles of energodynamics. In this regard the violation of the process distinguishability law immediately becomes evident. This violation is that the experimentally discovered specific spin-lattice relaxation qualitatively distinguishable and irreducible to other processes has been interpreted as heat exchange. This leads to "under-determinacy" of the system since instead of specific parameters of the spin-lattice relaxation to be introduced the parameters of thermal degree of freedom were used.

Meantime, in case of the spin-lattice interaction the matter of interest is not a heat exchange (i.e. an internal heat exchange between bodies spatially separated), but the energy redistribution by mechanical degrees of freedom of the same atoms in the LiF crystal lattice. The fact there is a certain connection between the heat form of motion and the spin orientation does not give ground to attribute this form to the spin system, the more so because cooling of condensed media down to the absolute zero does not lead to disappearance of the intrinsic rotational moment of nuclei. The existence of this interaction leads to non-conformance between the experimental conditions and the temperature concept definition in thermodynamics (13.1.1). In fact, according to (13.1.3) negative values of the thermodynamic temperature may be reached only when the system is converted, by reversible heat exchange, into a state featuring a higher internal energy U and a lower entropy S. Meantime, both known ways to reach the population inversion in the nuclear spin system (the external magnetic field inversion and the radio-frequency pulse action) do not comply with these conditions. In the first case the external magnetic field direction changes so fast, as Pursel stressed, that the nuclear spins have no time enough to change their orientation. Hence, the internal state of the system (including its entropy S) remained unvaried – just the external potential (Seemann) energy of spins in magnetic field entering in the Humiltonian function of the system along with the energy of spin-spin interaction changed. The system internal energy U, which by definition does not depend on the state of the system as a whole in external fields, remained unvaried in that case. Otherwise (if U changed), the condition would be violated that in expression (13.1.1) the coordinates of all kinds of work should be constant, but not just of volume. This refers to also the other way of the population inversion reachable with the help of the high-frequency (180-degree) impulse. This action can by no means be referred to heat exchange since it has also a directional nature and corresponds to the adiabatic process of external work done on the system.

Another remark concerns the question to what extent it is justified to attribute the entropy S to the nuclear spin system as its state coordinate. In thermodynamics the necessary condition of entropy existing in a system is known to be the availability of other states in the vicinity of the arbitrary state of this system, which are unattainable from it adiabatically. This statement known as the "adiabatic unattainability axiom" means the acknowledgment of the evident fact that a thermal interaction leads to such state variations which can not be attained by any other quasi-static way (I. Bazarov, 1991). Meantime, as the same Ramsey's experiments showed, the LiF crystals being cooled down to the liquid helium temperature, produces the same effect as the adiabatic demagnetization of the specimen. The "adiabatic unattainability" being absent in this case ex-

cludes the "mathematically most rigorous and coherent" system of the entropy existence substantiation (I. Bazarov, 1991) in application to spin systems. Thus we have one more example of discrepancy between the thermodynamic entropy and the statistical-mechanical entropy.

The most illustrative in this respect were quite complicated and delicate "mix" experiments on the two opposite-polarized spin systems (^{7}Li and ^{19}F) of the LiF crystals (A. Abragam, W. Proctor, 1959). Those experiments confirmed (to acceptable accuracy) the law of angular momentum conservation at the spin-spin interaction and showed the mix "temperature" defined by the expression:

$$T = (\Sigma_i C_i / T_i) / \Sigma_i C_i , \qquad\qquad (13.2.2)$$

where T_i – temperature of whatever part of the spin system; C_i – weight factor the experimenters named the "spin heat capacity". As follows from (13.2.2), the "spin heat capacity" C_i is referred to a value inverse to absolute temperature. Thus the mixing of spin systems with different "temperatures" does not at all obey the traditional conservation laws. On the contrary, the weighted average in (13.2.2) refers not to a temperature, but to its inverse value meaning in this case the nuclear magnetization $\mathbf{Z}_M$ and featuring the quite other degree of freedom of the spin system. This fact once again confirms the necessity of additional state variables to be introduced with a new degree of freedom revealed.

Anyway, it is not without reason that a number of investigators suppose the concept of spin temperature (positive or negative) lacks the physical meaning of thermodynamic temperatures and often misleads (A. Abragam, W. Proctor, 1959). Therefore the above interpretation of the said experimental results looks like rather a "some statement of laws of spin-temperature game" (M. Goltzman, 1972).

13.3. Non-Thermal Nature of Spin-Spin Interaction

As already noted above, the same experiments considered from the positions of energodynamics drive to a conclusion the spin-spin and spin-lattice interactions experimentally revealed are irreducible to heat exchange, but belong to a specific interaction class named *orientation* in Chapter 2. This interaction is caused by an orientation component of the system energy $E = E(\varphi_i)$, i.e. by its part dependable on relative position of the bodies. Different positions of a body in space and its different spatial orientations are known to be non-equivalent from a mechanical standpoint (L. Landau, E. Livshits, 1973). Unfortunately, the orientation component of the system energy $E = E(\varphi_i)$ has been hitherto studied with in-

sufficient care. This may be attributed to the fact that to solve many application problems, the laws of body motion have been more conveniently reduced to the laws of motion of particular material points which spatial orientation did not matter anymore. In that case it was enough to consider the so-called central fields which potential energy $U(\mathbf{r})$ depended on only the distance between the bodies (on the radius vector of center of their inertia $\mathbf{r}$). However, for rotating bodies and those with non-spherical symmetry the energy is defined by not only their position, but also orientation, i.e. $U = U(\mathbf{r}_i, \boldsymbol{\varphi}_i)$. This relates to the potential energy of particle interaction, which depends on the relative orientation of particle spins. This is the energy efficiency of a state with a certain relative spin orientation that predefines the nature of a number of chemical transformations (in particular, ortho- or parahydrogen formation) and explains ferromagnetism and anti-ferromagnetism). So in molecules with the covalent chemical bond (e.g. in the hydrogen molecules) that state is more energy-efficient where the spins of valence electrons in the bonding atoms are anti-parallel. In ferromagnetic, on the contrary, that state has lower energy where the spins of electrons in vacant shells of the adjacent atoms (and their magnetic moments) are parallel, which causes spontaneous magnetization. Therefore, when describing a number of macro-physical properties of substances, the processes of nuclear particle spin orientation (reorientation) running there must be taken into consideration. In energodynamics these processes are described by the last sum in equation of energy conservation (2.4.5). Their specific character is in this case that the ordered orientation of a nuclear spin subsystem is transferred to other one (including that with opposite orientation) and a single "weighted average" orientation of the two spin subsystems is set up. The specificity of such interaction is as well acknowledged by quantum mechanics, according to which the main part in the spin-spin equilibrium set-up belongs to some specific interaction attributed to the so-called *exchanged forces*. These forces become perceptible only when the mean particle-to-particle distance becomes comparable with the de Broglie wave-length. Their effect is manifested even in the case when the direct power (electric, magnetic) interaction between particles may be neglected. The nature of these forces is not yet discovered, however, this is not that important from the positions of energodynamics since for their definition the available relationship $U = U(\mathbf{r}_i, \boldsymbol{\varphi}_i)$ is sufficient. Now let us clarify how the spin systems will be described with the orientation degree of freedom taken into consideration.

13.4. Description of Spin Systems from the Positions of Energodynamics

Nuclear particles, when rotating, are known to undergo precession, i.e. a motion when the axes of their rotation make a spatially oriented angle φ_s with the external field vector $\mathbf{H}$. From a thermodynamic standpoint this means one more degree of freedom to be allowed for in the thermodynamic equation. This degree of freedom depends on not only the total intrinsic angular momentum of the nuclei in the substances under investigation $\mathbf{J}_s$, but also on its spatial orientation (angle φ_s). Depending on this angle, the spin projection $\mathbf{I}_s$ of the ith elementary particles on a chosen spatial direction (e.g. on the external magnetic field $\mathbf{H}$ direction) varies from $-\mathbf{I}_s$ до $+\mathbf{I}_s$ (which corresponds to $\varphi_s = 180^0$ and $\varphi_s = 0^0$). Hence the total angular momentum $\mathbf{J}_s$ is related to the spin $\mathbf{I}_s$ thru the relationship:

$$\mathbf{L}_c = \Sigma_i \, h\mathbf{I}_c \cos \varphi_c, \qquad (13.4.1)$$

where h – Planck constant.

Along with this, nuclei, atoms and molecules of condensed substances are known to possess some magnetic moment $\mathbf{Z}_M$ primarily caused by the orbital motion of electrons around nucleus and by their spins. Thus the internal energy E of condensed substances generally depends on not only their temperature (or entropy S) and magnetic moment $\mathbf{Z}_M$, but on also the relative orientation of spins (angle φ_s). The parameters S, $\mathbf{Z}_M$ and φ_s are in principle independent so that the energy E of condensed substances as the function of their state looks like $U = U(S, \mathbf{Z}_M, \varphi_s)$, while its exact differential is expressed by the relationship:

$$dU \equiv TdS - \mathbf{H} \cdot d\mathbf{Z}_M - \mathbf{M}_c \cdot d\varphi_c, \qquad (13.4.2)$$

where $T \equiv (\partial U/\partial S)$ – absolute temperature of the system; $\mathbf{H} \equiv (\partial U/\partial \mathbf{Z}_M)$ – external magnetic field intensity; $\mathbf{M}_s \equiv (\partial U/\partial \mathbf{J})$ – orientation moment. In this expression the term $\mathbf{M}_s \cdot d\varphi_s$ features the work associated with the orientation polarization of the nuclear spin system (as the term $\mathbf{H}d\mathbf{M}$ features the work associated with the system magnetization). From this, based on the exact differential properties, additional differential relationships follow in the form:

$$(\partial Z_{\alpha M}/\partial \varphi_{\alpha c})_\mathbf{H} = (\partial Z_{\alpha M}/\partial H_\alpha)_\varphi. \quad (\alpha = 1,2,3) \qquad (13.4.3)$$

According to this relationship the angle of orientation polarization φ_s of a nuclear spin system varies under the influence of the external mag-

netic field **H** inasmuch as the system magnetization $\mathbf{Z}_M$ – due to the spin system reorientation (angular momentum $\mathbf{J}_s$ variation). However, the magnetic field **H** being constant, the $\mathbf{Z}_M$ variation can be caused by just the variation of nuclear magnetization (dipole magnetic moment of nuclei) $\mathbf{Z}_n$ that is related to the total angular momentum $\mathbf{J}_s$ thru the so-called gyro-magnetic ratio γ_s:

$$\mathbf{Z}_n = \gamma \mathbf{L}_c , \qquad\qquad (13.4.4)$$

Then (13.4.2) may be substituted for:

$$(\partial \boldsymbol{\varphi}_c / \partial \mathbf{H})_{\mathbf{L}} = \gamma_c . \qquad\qquad (13.4.5)$$

Thus the orientation polarization of a nuclear spin system under the influence of external magnetic field really takes place and is expressed by the said gyro-magnetic ratio γ_s. The fact that both the left-hand side and the right-hand side of equation (13.4.3) differ from zero validates the idea of allowing for an additional degree of freedom associated with the spin system orientation. Thus the acknowledgement the orientation processes and the associated additional degree of freedom of condensed substances actually exist results in compliance with experiment. Thereby energodynamics eliminates the paralogism of negative absolute temperatures confirming once again the inviolability of the laws of thermodynamics.

Chapter 14

ELIMINATING PARALOGISMS OF RELATIVISTIC THERMODYNAMICS

In the years passed after the fundamental work of A. Einstein had appeared (1905) with a formulation of the special theory of relativity (STR) physicists endeavored to impart such a form to the classic laws that would be invariant in all inertial frames of reference. M. Planck was the first who declared that in thermodynamics (1907), while A. Einstein approved his transformations. However, then an event occurred rare for

physics – the Planck's transformations were discovered to have led to an absurd result half a century later. The subsequent lively discussions not only failed in reaching an univocal result, but showed up such a discord in definitions and interpretations of the basic concepts of energy, heat and work that a necessity appeared to completely shuffle up the fundamentals of thermodynamics. That circumstance was in that time one of the incentives to develop energodynamics. Energodynamics does not need relativity since it considers the entire set of interacting bodies as a system stationary on the whole and placed in the stationary space together with the observer. This enables analysing the relativity effects from the other positions. This chapter is dedicated to the situation arisen, which will be analyzed from the positions of energodynamics.

14.1. Ambiguity of Relativistic Transformations of Thermodynamic Values

According to the Lorentz – Poincaré – Einstein general theory of relativity all physical laws should be written in a form invariant with respect to any inertial frame of reference. M. Planck first revised the laws of thermodynamics from that standpoint (1907). He proceeded from the assumption that the first and the second laws of thermodynamics must remain as well valid for transformed values in an arbitrary frame of reference. Based on the expressions known in mechanics for transformation of the energy U and acceleration work $đW_w$ he came to a conclusion that the heat Q and absolute temperature T should be transformed in accordance with the expression:

$$Q' = Q\gamma \; ; \; T' = T\gamma \; , \qquad (14.1.1)$$

where Q', T' – heat and temperature in a reference frame moving relative to an observer with a velocity of $\mathbf{w}$; $\gamma = (1 - w^2/c^2)^{1/2}$ – Lorentz factor, c – velocity of light in vacuum.

As for the entropy S, it must, by Planck, remain lorentz-invariant since the uniform acceleration of all system parts refers to adiabatic processes. Those relationships were doubtless for all until 1963 when H. Ott discovered the absurdity of that result from a thermodynamic standpoint. In fact, accelerating a heat source (well) with a temperature of T_h up to a velocity of $\mathbf{w}$, using its heat Q'_h in the relativistic Carnot engine (with a fast moving heat well) and then decelerating it again to a velocity of $\mathbf{w} = 0$, the result of the said operations must exactly coincide with the work

done by the classic Carnot engine. This does not occur, though. To accelerate a heat well with an own weight of M, the work W_w' to be done corresponding to its kinetic energy increment $E^k = M' - M$, which, given the Einstein's relativistic formula $M' = M/\gamma$, is equal to $W_w' = Mc^2(1/\gamma - 1)$. After rejecting the heat Q'_h from the heat well its own weight will vary by the value $\Delta M = Q'_h/c^2$ and when decelerating the heat well the work $W_w'' = (Mc^2 - Q'_h)(1/\gamma - 1)$ will be restored. From this it follows that to accelerate the heat well and to decelerate it, the work will be done as

$$\Delta W_w = W_w' - W_w'' = Q'_h(1/\gamma - 1). \qquad (14.1.2)$$

Subtracting this work from the work W_c' gives:

$$W_c = Q_r(1 - T_x/T_r) - Q_r\,(\gamma - 1/\gamma). \qquad (14.1.3)$$

This result does not correspond to the classic expression $W_c = Q_h(1 - T_c/T_h)$, which evidences incorrectness of the Planck's transformations. Therefore Ott proposed other transformations for heat and work:

$$Q' = Q/\gamma\;;\;\; T' = T/\gamma\,, \qquad (14.1.4)$$

which allows eliminating this discrepancy.

The difference between the Planck's and Ott's transformations is referred to the equivocal definition of the accelerating forces (Möller, 1970). In fact, when deriving the relativistic equation for work, Planck used the force as a momentum derivative:

$$\mathbf{F}_w = d(M\mathbf{w}_m/\gamma)/dt, \qquad (14.1.5)$$

which includes the system weight (mass) under the derivative sign. However, H Otts applied the following expression to the force:

$$\mathbf{F}_w = Md(\mathbf{w}_m/\gamma)/dt\,. \qquad (14.1.6)$$

The distinction between those two are that expression (14.1.5) and (14.1.6) contains an additional "Planck's force" appearing in calculations, which is necessary to maintain the constant velocity of a body being heated and the associated increment in the rest mass. This force has a number of unusual properties (does not obey the conventional force transformation rules) and lacks distinct physical meaning. However, thanks to this force the law of action and reaction equality coincides with the law of conservation of momentum. Besides, the interpretation of electromagnetic phenomena is facilitated. The distinction between expressions

(14.1.5) and (14.1.6) naturally affects also the relativistic transformation of heat which, failing an independent definition, is usually defined "by inverse balance" (i.e. as "what is not work").

The H. Ott's article passed unheeded when alive. However, H. Arzelies came to the same conclusion (1966) apart from Ott. Unlike Ott, he treated as wrong also the energy and momentum transformation formulae ensuing from relativistic mechanics of elastic bodies. That time the work was heeded and an avalanche of publication followed having led to a lively discussion at the international symposiums in Brussels (1968) and Pittsburg (1969). Those discussions revealed indiscrete chaos in the definitions of fundamental notions and concepts of thermodynamics, which gave H. Arzelies grounds to announce the current crisis of thermodynamics. The point is not just in the absence of unity between the relativistic transformations of energy, heat and work, but rather in investigators' reluctance to apply to the fundamentals of thermodynamics each time the necessity arises to generalize its methods to a more general class of systems. This shows, in particular, in the works appeared, which authors endeavor to "reconcile" different transformations. They propose "combined" expressions for the heat Q' voluntarily going over into either (14.1.1) or (14.1.6). Some go so far as to declare that the application of each of the formulae depends on the spatial position of thermometer (I. Bazarov, 1983). Meantime, this is a consequential decision since the available contradictions directly threaten the status of thermodynamics as a theory most logically consistent and mathematically rigorous.

14.2. Non-Invariance of Expression for Efficiency of Relativistic Carnot Cycle

The discordances arisen in relativistic thermodynamics touch not only the methodological aspects of thermodynamics, but also the fundamental consequences of the heat engine theory and the law of excluded perpetual motion of the second kind. Following the M. Planck's reasoning the relativistic Carnot engine may be imagined as a cylinder with a gas under the piston. Its operation differs from that of the classic Carnot engine in just the acceleration of working medium after its adiabatic compression and in the deceleration after receiving the heat Q'_h from a moving heat well. Let us choose such a frame of reference where the heat sink (receiver) is at rest. Let a gas-containing cylinder first be moving along with the heat well receiving from it a heat of Q'_h at a temperature of T_h'. Then the gas-containing cylinder is adiabatically decelerating to rest and the gas temperature becomes equal to T_h. The gas in the cylinder is subsequently ex-

panding to the temperature T_c of the heat sink giving it some heat Q_c at a temperature of T_c and then adiabatically compressing again to the temperature T_h. After that the gas-containing cylinder is again accelerating and the cycle repeating. Due to the entropy invariance evident equalities are observed for such a cycle:

$$Q'_\text{г}/T_\text{г}' = Q_\text{г}/T_\text{г} = Q_\text{х}/T_\text{х} . \qquad (14.2.1)$$

The work W_c' done in the relativistic Carnot cycle is equal to

$$W_\text{ц}' = Q'_\text{г} - Q_\text{х} = Q_\text{г}(1 - T_\text{х}/T_\text{г}') = Q_\text{г}(\gamma - T_\text{х}/T_\text{г}). \qquad (14.2.2)$$

Herefrom, given (10.1.1) and (10.1.2), the expression follows for the thermal efficiency of the relativistic Carnot cycle (M. Planck, 1907):

$$\eta_t^\text{K} \equiv W_\text{ц}'/Q'_\text{г} = 1 - T_\text{х}/T_\text{г}\gamma . \qquad (14.2.3)$$

Thus the Planck's transformations did not allow for invariance of the Carnot cycle efficiency η_t^C which expression is one of the mathematical formulation of the second law of thermodynamics. By Planck, the temperature of a moving heat well is always below the one measured in a stationary frame of reference, and according to his transformations the relativistic Carnot cycle efficiency (14.2.3) is always below the classic one. And what is more, at certain γ this efficiency may appear even negative. On the contrary, by Ott, the temperature of a moving heat well is always higher, and his Carnot engine has the efficiency higher than that of the classic engine:

$$\eta_t^\text{K}{}_\text{(Отт)} = 1 - T_\text{х}\gamma/T_\text{г} . \qquad (14.2.4)$$

From this it follows that even with the heat well and heat sink temperatures being equal in the own frame of reference the Ott's engine will do work. At $\gamma \to 1$ the efficiency of this engine will approach unit irrespective of the heat well and heat sink temperatures. The non-invariance of thermal efficiency for the ideal Carnot cycle, which features one of the most fundamental laws of nature, viz. the law of excluded perpetual motion of the second kind, looks like evident paralogism, especially granting the fact that this conclusion has been made as proceeding from the invariance of all laws of nature (including the first and the second laws of thermodynamics) in any inertial frame of reference. That is why it looks reasonable to discuss this issue from more general positions of energodynamics.

14.3. Relativistic Carnot Engine as Compound Engine

The contradictions arisen can be partly settled with a more general definition of absolute efficiency of heat and non-heat engines (see 10.3.5) receiving energy from several sources of various nature:

$$\eta_i = W_j / U_i' = 1 - \Psi_i'' / \Psi_i'. \qquad (14.3.1)$$

For this let us first make sure that the relativistic Carnot engine is not merely a heat engine. In fact, the working medium of such an engine receives, along with the heat Q'_h, also the kinetic energy $E^k = Q'_h(1/\gamma_h - 1)$ required to maintain its velocity during the heat absorption and the associated rest mass increasing $\Delta M = Q'_h/c^2$. Therefore such an engine is a combination between a merely heat engine doing the work W_t owing to the heat well Q'_h and a mechanical engine doing the work W_w owing to the kinetic energy E^k received from the heat well in the course of heat absorption. This work of the heat sink generally moving will be defined by the expression:

$$W_w = \Delta E^\kappa = \Delta M \, (c^2/\gamma_h - c^2/\gamma_c), \qquad (14.3.2)$$

where $\gamma_c = (1 - v_c^2/c^2)^{\frac{1}{2}}$; v_c – relative velocity of heat sink.

Thus the efficiency of such a "compound" engine must be defined as:

$$\eta_{(t+w)} = (W_t' + W_w)/(Q'_h + E^\kappa) = \eta_t \, \gamma_h + \eta_w \, (1 - \gamma_h),$$

(14.3.3)

where

$$\eta_t = W_r' / Q'_h; \quad \eta_w = W_w / E^\kappa = 1 - \gamma_h/\gamma_c \qquad (14.3.4)$$

– absolute efficiencies of, respectively, the Carnot merely heat engine with the moving heat well and the "kinetic" engine doing useful work due to deceleration of the working medium with a mass increased in the course of heat absorption. It can be easily seen that the efficiency of such "compound" engine (10.3.2) is "weighted mean" of η_t and η_w, i.e. takes an intermediate value tending to η_t at $\gamma_h \to 1$ and to η_w at $\gamma_h \to 0$. This result meets the correspondence principle since in the particular cases considered we deal with the merely heat and merely mechanical engine. Thus one of the reasons of the confusions arisen refers to the arbitrary extrapolation of the heat engine concept to systems with fast-

moving heat wells. However, the contradictions relating to the relativistic transformation of thermodynamic values remain unsolved.

14.4. Inapplicability of Relativity to Absolute Values

The approaches of classic mechanics and classic thermodynamics to studying the surrounding world phenomena are diametrically opposite in some respects. Mechanics of conservative systems (unlike the "synthetic" theories such as hydromechanics, thermomechanics, continuum mechanics, etc) does not consider the internal processes occurring in moving bodies. It does not contain the notion of internal energy U in its arsenal, while the energy conservation law, as applied to it, means the total constancy of the external kinetic $E^{\text{к}}$ and external potential $E^{\text{п}}$ energies:

$$(E^{\text{к}} + E^{\text{п}})_{\text{isol}} = \text{const.} \qquad (14.4.1)$$

Classic themodynamics, on the contrary, studies the internal processes occurring in various media and, therefore, operates the notion of internal energy U. Thus the energy conservation law therein

$$dU \equiv \Sigma_i \Psi_i \, d\Theta_i \qquad (14.4.2)$$

does not contain the components $\mathbf{F}_i$, $\mathbf{r}_i$ of the external energy that, by definition, does not depend on the body internal state (temperature, pressure, chemical etc potential). Whereas energy in mechanics is defined by the motion or position of a particular system relative to other bodies (reference systems), i.e. is relative, the same in thermodynamics, on the contrary, does not depend on whatever external bodies[1], i.e is absolute.

The attempts to combine these mutually exclusive concepts in a number of the "synthetic" theories considering the variation of both external and internal energies results in a whole number of paralogisms as shown above. Here also comes the Einstein-approved Planck's attempt to introduce relativistic corrections to classic thermodynamics.

To avoid them, energodynamics provides for the possibility of uniting the subsystems possessing external (mutual) energy into a single nonequilibrium "extended" system thus converting the external energy into the ordered component of its internal energy. In the most general case such a system is closed, confined and isolated with its center fixed. The application of the relativity theory for such a system is superfluous.

All conclusions following from relativistic mechanics relate to moving material point or body with invariable rest energy U depending on exclusively rest mass M and a known relation $U(M) = Mc^2$ associated

with it. Let us consider how all these conclusions would change with the entire set of interacting (relatively moving) material bodies considered. Such an object is by definition an isolated and closed system with all its energy U being self-energy (intrinsic). Intrinsic energy of a system is defined as that part of its total energy which does not depend on position or movement of the system relative to other bodies, but is conditioned by exclusively its internal properties. It follows from this definition itself that intrinsic energy of a system is its Lorentz-invariant value independent on velocity the system is moving with relative to whatever reference system. What argued in favor of the relation $U' = U/\gamma$ known from relativistic mechanics and usually taken for the intrinsic energy relativistic conversion formula (R. Tolman, 1974)? Such a conclusion appears to be usually drawn based on the following simple reasoning. Let two bodies with a mass M and self-energy U each move toward each other with a velocity **w**. Then, at the moment their relative rest occurs, their kinetic energy $E^k = (M' - M)c^2$ converts into internal energy (thermal at elastic collision and potential at inelastic one). Then the inertial mass $(M' - M)$ transforms into the rest mass ΔM, which results in increase in the self-energy $U(M)$:

$$U(M + \Delta M) = U(M) + Mc^2(1/\gamma - 1) = U/\gamma . \qquad (14.4.3)$$

This relation characterizes, however, nothing but the dependence of self-energy on rest mass which has changed here due to the conversion of external energy into internal one. This not at all means that the self-energy has become a velocity **w** function. In the similar way the rest mass will change when external energy of a body transforms into its self-energy. In other words, equation (10.4.1) expresses self-energy variation due to rest mass variation whatever reasons would cause it. In this case any other bodies' relative velocity function different from the Lorentz formula might take the place of the factor γ. So a logical error is present here as rooted in a substitution for argument of function or, more generally, for the philosophic categories of essence and phenomenon.

The necessity in relativistic internal energy conversion is equally as often argued for by body volume variation due to the Lorentz dimensional reduction in the direction of movement. At mechanical equilibrium with the environment such a volume variation involves cubic strain work done, which allegedly causes the internal energy variation. However, such an "argumentation" is inconsistent, too, since a reduction in dimensions in the direction of movement can be easily neutralized by the adequate dimensional variation in the transversal direction leaving the body volume V invariable. Furthermore, the said reduction in dimensions takes place in also vacuum, where expansion work is not at all done.

The necessity in relativistic internal energy conversion is often argued for by variation of system parameters due to system acceleration. In particular, it seems to be rather natural that the temperature of a body decreases with the velocity of the system approaching the velocity of light, because this temperature is, like entropy, a measure for energy of chaotic motion particles are involved in, which gradually gives way to ordered motion of the body as a whole. In the special theory of relativity (STR) transformations do not depend on whether a system is moving relative to an observer or the observer is moving relative the system. Therefore it is quite admissible to consider a body as stationary (with its inherent chaotic motion), whereas the reference system – as movable with relativistic velocity relative to the body. In such a case the system status ordering will be nothing but apparent for the moving observer, while using the Lorentz transformations will be aimed at reducing measurement results to those observed in the inherent reference system. The same problem is to be solved when the true nature of phenomena observed is considered. E.g., the observer moving together with permanent magnet relative to stationary conductor would, according to STR, attribute the current generated therein to the action of merely magnetic forces. On the contrary, should conductor move relative to magnet, he would consider this phenomenon as nothing but electric (R. Feynman, 1977). Such ambiguity would disappear if the investigator studied the entire set of moving bodies in inherent reference system considering it as a single whole. Such a reference system (absolute) would make it possible to find the true nature of acting forces.

It may be easily instantiated how far the STR conclusions differ from energodynamics. Assume some two domains of an isolated system with the same mass m start relative motion. Then according to the relativistic relation between mass and energy $m' = m/\gamma$ and the law of mass conservation for isolated system as a whole the increment of inertial mass by a value of $2(m' - m) = 2m(1/\gamma - 1)$ will be provided at the expense of the equal decrement of the system rest mass $M - 2m' = M - 2m/\gamma$. Equating these mass variations gives:

$$\gamma = 4m/(M + 2m). \qquad (14.4.4)$$

According to (14.4.4) at $m > 0$ it is *impossible* to reach the velocity v $= c$ ($\gamma = 0$) in whatever domain of the system. Meanwhile, from astrophysics the total mass of photon flux moving with the velocity of light in the Universe is not at all equal to zero. This example evidences that STR based on the Lorentz transformations is in principle inapplicable to isolated systems. The reason is clear: no domain of a system can acquire infinite mass if provided at the expense of finite masses of other system

domains. So if considering not a material point (as in STR) as a system, but an isolated system in whole and using the mass-on-velocity dependence ensuing from STR, it is not so hard to discover STR nonconformance with experiment.

With such an approach it is equally as easy to make sure of inadmissibility to apply relativistic transformations for also any state parameters being arguments of self-energy U as a state function for isolated system. Let us consider for this purpose some isolated system, which separate domains are moving with relativistic velocities relative to stationary center of gravity. As shown above (Chapters 1 and 2), the state of such a system is characterized by a certain set of variables Θ_i and $\mathbf{r}_i$ or $\mathbf{Z}_i$, i.e. $U = U(\Theta_i, \mathbf{r}_i)$. Then according to the general definition of generalized potential $\Psi_i \equiv (\partial U/\partial \Theta_i)$ any of them stays invariable at any relative motion of the system domains since their displacement influences the variables $\mathbf{r}_i$ only. Hence neither the mean temperature of the system nor its mean pressure vary in relative motion of domains of the isolated system. This fact confirms the conclusion made in Chapter 3 of the necessity to measure any of potentials in absolute scale which zero corresponds to complete degeneracy of this kind of interaction. Apropos the necessity to find absolute scales of potentials was first realized yet in fluid mechanics as applied to pressure. With classic mechanics a necessity appeared to know absolute temperature T and with changing to open system – also entropy S. Now we are in a position to show that this requirement concerns not entropy only, but any parameters Θ_i. To do so, it is enough to consider the generalized expression for ordered work $đW_i^e = \mathbf{X}_i \cdot d\mathbf{Z}_i$. Since $\mathbf{X}_i \equiv -\nabla \psi_i$, $d\mathbf{Z}_i = \Theta_i d\mathbf{r}_i$ and $(d\mathbf{r}_i \cdot \nabla)\psi_i = d\psi_i$, then $đW_i^e = -\Theta_i d\psi_i$, so that the unique definition of energy conversion quantitative measure requires to measure any parameter Θ_i in absolute scale independent on the nature of measuring substance and values of other system parameters. Thus the necessity to measure the generalized potentials ψ_i and generalized coordinates Θ_i of any processes ensues from the law of energy conservation (for energy transfer and energy conversion, respectively). This relates to the system energy U itself, too, as the function of these variables.

This fact entails the invariance of heat Q and work W, which is quite natural, since each of them separately features the variation of self-energy as an invariant value. The invariance of specific self-energy, entropy and volume results as per (14.4.1) in the invariance of thermal efficiency of Carnot cycle.

However, energodynamics allows advancing even further. Considering the entire set of interacting (relatively moving) bodies as a single whole allows finding an absolute scale for also velocity. Absolute velocity in such a system is defined relative to center of inertia of the homoge-

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neous isolated system, which position can be changed by no means. While measuring such a velocity is problematic, the fact of its availability as itself is significant.

Being a deductive discipline, energodynamics considers rotating systems in the most general case. For rotational motion a primary reference system is known to be available – this is the center-of-inertia system (L. Landau, E. Livshits, 1973). With respect to such systems the Poincaré–Lorenz–Einstein's idea of the invariant interpretation of physical laws is not just inapplicable as itself, but actually contradicts the special relativity theory and the general relativity theory. Indeed, according the relativity theory it does not matter whether the Earth is rotating relative to the Universe or the Universe is rotating relative to the Earth. However, in the latter case we have to assume the supraluminal speed of motion for all parts of the Universe! This narrowness of the generalized relativity principle bereaves it of whatever heuristic value and puts forward as more preferable those reference systems wherein physical laws look like especially simple. This statement is reasonable to be called for easy reference as the **absoluticity principle**: *there are preferable frames of reference whererin the laws of physical phenomena look especially simple and do not depend on the observer's state of rest or motion.* In this respect energodynamics may be considered as an "absoluticity theory". It hardly needs proving that the absolute values energodynamics operates differ from relative ones because they do not depend on the state of any external bodies, including the observer's state of rest or motion.

It hardly needs proving that absolute values differ from relative ones just because they do not depend on the state of any outside bodies including the movable status of the observer. This fact draws the final line under the issue of relativistic transformations of thermodynamic values and supports the idea the academician I. Tamm (1956) expressed, "none can certainly foresee what further development of physics would be, but one thing, as it seems to me, could be certainly affirmed – the ideas of Einstein, his analysis of the concepts of space and time and space-time relations interacting with the matter existing in space and time could undergo fundamental changes in the future".

Conclusions to Part 3

When considered from more general positions a number of thermodynamic generalizations not supported with any correction of thermodynamic concepts and laws reveal paralogisms in each of the applications of

thermodynamic jeopardizing its status as a theory logically immaculate and immutable in its deductions. These paralogisms are caused by the fact that the classic thermodynamic method based on the equilibrium and reversibility concepts has been drawn out of the strict framework of its applicability. Additional non-equilibrium state variables having been denied in the investigation of spatially heterogeneous media and systems with additional degrees of freedom, heavy consequences followed. Those manifested themselves in reducing the idea of excluded perpetual motion to exclusiveness of hot well properties, in acknowledging the "inversion" of the law of excluded perpetual motion in the systems with negative absolute temperatures, in non-invariance of the relativistic Carnot cycle efficiency, in denying a thermodynamic solution to the problem of thermodynamic inequalities, in enduing negentropy with the properties of system-degree-of-order measure, in absolutization of a entropy increase principle and distorting the relation of thermodynamic entropy with dissipation and irreversibility, in extrapolating the law of entropy rise to the entire Universe, in applying the theory of relativity to absolute values, etc. Especially heavy consequences appeared as a result of statistical treatment of entropy and departure from the methodology of thermodynamics for open systems, which showed in inadequacy of the material equilibrium criteria, in substituting the conditions of TIP stationarity for those of material equilibrium, in loosing the free energy properties as potential, in denying the applicability of the law of excluded perpetual motion to such systems, etc. Elimination of these contradictions confirms the inviolability of thermodynamics within the framework of its laws' validity and opens up new vistas in further extension of the applicability of thermodynamic methods.