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THERMOKINETICS

(SYNTHESIS OF HEAT ENGINEERING THEORETICAL GROUNDS)

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V.A. Etkin . THERMOKINETICS (Synthesis of Heat Engineering Theoretical Grounds).

The book calls attention to a method of describing and investigating various physicochemical processes in their inseparable link with the heat form of energy. The method is based on the law of energy conservation and free of hypotheses and postulates.

All the basic principles, laws and equations of equilibrium and non-equilibrium thermodynamics, heat- and mass-exchange theory, thermo-economics and thermodynamics of finite-time processes are here derived from this method as particular cases.

The book considers also with much attention phenomena at the interfaces between heat engineering and other engineering disciplines, elaborates new applications of the energy transfer and conversion theories, as well as analyzes paralogisms arising in thermodynamics due to its inconsistent extrapolation.

The book is intended for researches, engineers and university students keen-set for updating, extension and integration of knowledge in heat engineering disciplines. It may be useful also for a wide audience interested in issues relating to perfection of the modern natural science conceptual frameworks.

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INTRODUCTION

No sooner had the heat theory appeared, it immediately bifurcated into two branches. In 1822 a known J. Fourier's work appeared, which laid the foundation of the heat transfer theory; in 1824 not less famous S Carnot's work laid the foundation of thermodynamics. Both works were based on the afterward-rejected theory of thermogen as the indestructible fluid, both considered temperature as some potential which gradient conditioned the heat transfer direction or conversion of heat into ordered forms of . However, both branches mentioned developed quite independently without any points of contacts. Their difference showed up not only in terminology, but it rather rooted in a basic methodological nature. Carnot-Clausius' thermodynamics maintained aloofness from the transfer ideas and the heat exchange rate concept. The heat exchange theory, on the contrary, had nothing to do with the conversion of heat into other forms of and considered entropy as an extraneous concept. The so "fancy separation of two branches within the same area in macroscopic physics" (to K. Denbigh's locution) was too hard to be overcome by the TIP as well. Even today the definition of heat concept remains different in thermodynamics and the heat exchange theory. In thermodynamics this is the part of exchange caused by exclusively the temperature difference between bodies and not associated with substance exchange between them (Thermodynamics. Terms, 1973). The heat exchange theory, on the contrary, considers heat as the part of internal associated with random motion (because a system can exchange just what it has) and studies, along with heat conductivity, the heat transfer carried out by substance and enabled by heterogeneity of the fields of other physical values (Heat Transfer. Terms, 1980). Such a situation demands searching more cardinal means to unify the two said fundamental disciplines.

Further, the growing comprehension of the fundamental role the rate and productivity play in real processes as one of the basic indices of their efficiency gave rise to two new branches in thermodynamics of the XX century called thermodynamics of irreversible processes (TIP) (Onsager, L., 1931; Prigogine I., 1947, 1955; Casimir H., 1945; Denbigh K., 1951; De

Groot S., 1952, 1962; Meixner I., 1954; Gyarmati I., 1960, 1970; Haase R., 1962, et al) and finite-time thermodynamics (Curson F., Ahlborn B., 1975; Rubin M., 1979, 1980, 1983; Andresen B., Salamon P., Berry R., 1977, 1980, 1982, 1984; Band Y.B., Kafri O., 1981; Rozonoer L., Tsirlin A., 1983; Linden C., 1992, et al), respectively. The first of the branches involves time as physical parameter introduced into the thermodynamic equations and a new macrophysical method developed on this basis for investigating kinetics of interrelated transfer phenomena. This branch has enriched the theoretical conception of the XX century with a number of new principles of general-physics meaning (including those of linearity, reciprocity, minimal entropy generation) and evidently contributed into cognition of the in-depth interrelations between dissimilar phenomena. However, TIP basing on the entropy rise law is restricted to investigating *dissipative processes* such as thermal conduction, electrical conduction, diffusion, as well as effects of their superposition, but has nothing to do with the issues of *productivity of useful conversion processes* which are the principal object of thermodynamics. As a result, the broadest spectrum of irreversible processes with a relative efficiency above zero appeared to have fallen beyond cognizance of this theory. The second branch, on the contrary, sets as a top-priority task the definition of the conditions to achieve maximum *useful* of cyclic heat engines with due consideration given to the irreversibility of heat exchange processes and finite-time contact between a working media and heat wells and sinks. Within the frames of this theory the problem has been posed for the first time and in the most general form about the relation between the capacity (productivity) of engineering systems and their thermodynamic efficiency, as well as about the critical capabilities of irreversible processes. However, this theory in its existing configuration is restricted to units wherein the operation at maximum power conditions is economically most advantageous. Though the spectrum of such units is broad enough (includes nuclear power plants, renewable plants, space vehicle power plants, etc), it does not include a number of power and process units wherein maximum of their efficiency does not correspond to maximum power. In this context a necessity arises to synthesize the said branches and create on this basis *thermokinetics* as a unitary theory of rate and productivity pertaining to transfer and conversion processes, which would cover the entire spectrum of real processes and occupy the same position relative to the classic theory of heat engines as dynamics to statics.

The necessity to create a division of thermodynamics supplementing the classic theory of heat engines with the *analysis of interrelation between thermodynamic efficiency and productivity (net capacity) of various kinds of converters (cyclic and non-cyclic, heat and non-heat)* is dictated by logic of the development in many fields of knowledge. Kinetics of useful conversion processes is a concern to not only power engineering and power processing wherein these processes are principle. The thermodynamic investigation of biological systems is also impossible without catering for work supporting the non-equilibrium state of such systems and providing their vital activity. The application of thermodynamics to cosmological objects that develop, according to current ideas, bypassing equilibrium would also be incomplete without work considered as ordered form of exchange. This refers to also antirelaxation phenomena observed under regular conditions at superposition of dissimilar irreversible processes (superposed when running simultaneously in the same spatial areas) and studied by synergetics.

The practicability to revise the grounds of thermokinetics in this case is dictated by the well explainable wish to avoid application of whatever hypotheses and postulates preventing TIP from achieving the completeness and rigor incident to the classic thermodynamic method. The acuteness of the problem intensifies with the necessity to overcome the certain restriction of the theory of irreversible transfer processes to linear systems and states close to equilibrium.

The thermodynamic theory of real processes of transfer and conversion in spatially heterogeneous media offered to the reader features a system approach to the theory construction (from the whole to the part), the exclusion of whatever hypotheses or postulates from theory grounds (like the "local equilibrium principle" or the "beginnings" of the classic theory of heat engines) and the negation of the traditional idealization of processes (their "quasi-static character" and "linearity", ideal character of cycles and their working media, etc). This theory is based on exclusively the empirical facts that underlie the law of conservation and the representation in terms of state parameters of systems under investigation. All other information about an object under investigation thermokinetics attributes to uniqueness conditions. The phenomenological and deductive theory of such a kind keeps undisturbed the key advantage of the classic thermodynamic method, viz. the immutable validity of its consequences. This is confirmed in the book by the fact that all the basic principles, laws and equations pertaining to equilibrium and non-equilibrium thermodynamics, as well as to the heat-mass exchange theory, which have gained multiple experimental verifications – all have been therein obtained as particular cases of thermokinetics under adequate uniqueness conditions. This allows, on its base, not only to correctly interpret various phenomena at the interfaces between thermodynamics and mechanics, physical chemistry, hydrodynamics, electrodynamics, biophysics, astrophysics, economics, etc, but also to predict new effects arising at the superposition of processes these disciplines study. It is significant that such an application of thermodynamics does not require a preliminary study of the above disciplines, neither of statistical physics on which base the TIP key principles have been earlier obtained. This allows a pathbreaking study of phenomena at the interfaces of fundamental disciplines as a unitary academic course of thermodynamics.

Much attention is given in the book to analyze and eliminate the paralogisms arising in thermodynamics from its unreasonable extrapolation beyond the primary concepts of equilibrium and reversibility, as well as to obtain a great number of other nontrivial consequences following from the consideration of spatially heterogeneous media as a unitary non-equilibrium whole. Besides, the book lays the foundations of two new applications of thermodynamics, viz. the theory of similarity and the theory of productivity of conversion systems, wherein a wide step is made on the way approximating the results of their thermodynamic analysis to reality.

The book offered to the reader consists of five parts. Part 1 – Methodological Principles of Thermokinetics (Chapters 1, 2) – describes the features of thermokinetics as a single to date scientific discipline free of hypotheses based on exclusively the law of conservation of and its representation in terms of measurable (or calculable) parameters of non-equilibrium systems being investigated.

While keeping the advantages of thermodynamics as a consistently phenomenological (i.e. exclusively empirical) and strictly deductive (i.e. developing from the general to the special) scientific discipline thermokinetics at the same time excludes from its grounds whatever postulates (like the “beginnings” of classic thermodynamics) and negates the idealization of processes and systems when constructing theory grounds and substantiating theory laws. Whatever simplifying assumptions are admitted here at only uniqueness conditions thermokinetics imports from outside at the final investigation stage when solving particular problems.

Unlike thermodynamics which is substantially thermostatics, thermokinetics as a generalized theory of heat transfer and conversion process rate is built on an extremely general notional and conceptual base not alien to the transfer and real process productivity concepts. The irreversibility of such processes is here catered for by introducing specific *spatial heterogeneity parameters* varying arbitrarily with relaxation of a system like entropy, but, unlike entropy, varying with also reversible work the system does. A rather simple way to find these parameters if offered, which pioneers the thermodynamic description of spatially heterogeneous systems as a whole.

The major feature of the thermokinetic notional system is that the is brought back to its simple and clear primordial meaning as a capacity of a system to do work. This is obtained by generalizing the notion of work and defining it as a quantitative measure of a process associated with overcoming any (long-range and short-range, ordered and unordered) forces. The further division of into its ordered and unordered parts and introducing for those characteristic functions as expressed by various groups of parameters for systems under investigation enabled the quantitative and qualitative description of system order and convertibility of in various forms. Such a generalization of the thermodynamic method of potentials allowed suggesting criteria of evolution and partial equilibrium much more informative than entropy and having a body of mathematics for thermokinetics equally applicable for study of processes with any irreversibility degree.

Part 2 – Heat Engineering Fundamentals (Chapters 3-5) – describes the application of mathematical and notional tools of thermokinetics in order to substantiate all basic principles, laws and equations of the heat engineering disciplines – classic and non-equilibrium thermodynamics, as well as the heat- and mass-exchange theory. The methodologically unitary exposition of all mentioned disciplines as consequences from thermokinetics is the most important result of this part. This approach eliminates the historical delimitation of thermodynamics and the heat-exchange theory as expressed in not only terminology and different interpretation of the transfer substrate, but in the methodology of these disciplines as itself. At the same time the book is a pioneer work to provide a consistently thermodynamic (with no recourse to hypotheses, postulates and statistical-mechanical considerations) substantiation of all statements pertaining to the theory of irreversible processes generalizing the heat-exchange theory to the associated phenomena of substance, charge, momentum, etc transfer. Thus a real possibility opens to include this subdivision of thermodynamics – fresh and implying multiple applications – into academic curriculums, which is a telling contribution to solution to the problem of scientific knowledge integration.

Part 3 – Elimination of Negative Consequences of Thermodynamics Extrapolation (Chapters 6-10) – exposes the contradictions arisen in thermodynamics because of its ungrounded extrapolation beyond the validity of its primary concepts pertaining to equilibrium and reversibility. Here come, in particular, the conclusion of inevitable “jump” of entropy when mixing non-interacting and however poorly distinguishable gases (Gibbs’ paradox); the appearance of thermodynamic inequalities when coming on to irreversible processes; the conclusion of violated law of excluded perpetual motion of the second kind in open, spin, relativistic, etc systems; the extension of the ban on environmental heat usage to non-heat forms conversion; the extrapolation of the entropy rise principle to the Universe resulting in the theory of “heat death” of the Universe; the application of the relativistic transformation to absolute values; the introduction of negative absolute temperature; the substitution of statistical-informational entropy for thermodynamic one; the statement of the heat conversion laws as exclusive; the attempts to apply the theory of dissipative processes to anti-relaxation structuring in biological processes, etc. It is shown here that such deductions are actually paralogisms, i.e. unintended logical errors caused by inconsistent extrapolation of classic thermodynamics. In each case the sources of the difficulties arisen are exposed and the way is pointed out how to overcome them from the positions of thermokinetics.

Part 4 – Further Generalization of Heat Engine Theory (Chapters 11-13) – presents new results obtained from application of thermokinetics to conversion processes in heat engines. The results include the theory of conversion processes similarity generalizing the theory of heat engines to non-heat and non-cyclic ones (including the muscular movers of bio-organisms); the theory of engineering systems productivity combining thermodynamics with two new fields of its application, viz. "thermo-economics" and "finite-time thermodynamics". The major result of such an approach is the substantiation of the possibility to use field forms of differing from its material sources. This opens up new vistas in creating machines on renewable sources being now erroneously attributed now to the category of "perpetuum mobile".

The last part (Part 5) of the monograph – Extension of Transfer Theory Applicability (Chapters 14-16) – generalizes the existing theory of irreversible processes to non-linear systems and states standing far from equilibrium. A new method is offered for investigating multiple thermo-mechanical, thermo-chemical, thermo-electrical, etc phenomena caused by "superposition" of dissimilar transfer processes in poly-variant systems and being of great practical interest. The method neither cumbersome equations of entropy balance nor application of reciprocal relations (violated in non-linear systems) while resulting in simplified transfer laws and further reduction of empirical coefficients they contain. This part also describes the application of thermokinetics to bio-systems exposing a special role of useful conversion processes in functioning of bio-systems – contrary to the existing ideas of their anti-entropy character.

All the said along with the methodologically unitary exposition of heat engineering fundamentals confirms the uniqueness and heuristic value of thermokinetics as a pro-thermodynamic method of investigating multi-functional systems completely based on system approach.

Part 1

THERMODYNAMICS AS THEORETICAL BASIS OF HEAT ENGINEERING

Each independent scientific discipline features its own subject and method. Thermokinetics may be considered as a basically thermodynamic method of investigating real processes of energy transfer and conversion in any forms being in inseparable link with the heat form of motion.Being consistently deductive, this method meets the system approach requirements with studying a part through the whole as one of them. That allowed classic thermodynamics to obtain, based on few primary principles ("the beginnings"), a great number of consequences covering various phenomena and having the status of oracles within the applicability of its primary concepts. That imparted an exclusive position to thermodynamics among a number of other scientific disciplines. However, when changing to studying non-equilibrium systems with irreversible processes running therein such an approach gave place to the inductive investigation method adopted in classic mechanics and a number of other fundamental disciplines. Continuum was divided there into elementary parts which may be considered locally equilibrium. The method assumes the possibility to study the whole through its elementary parts by summarizing their extensive properties. However, system-forming properties of real objects are basically non-additive. Therefore the theory of irreversible processes as a substitution for classic thermodynamics has essentially denied the system approach and has not gained the completeness and rigor inherent to the classic thermodynamic method.

The intention to keep the advantages of the thermodynamic method when generalizing it to non-thermal forms of energy and non-static processes impelled us to base thermokinetics on the same methodological principles of the consistently phenomenological and deductive theory as classic thermodynamics. However, we have based thermokinetics not on the laws of excluded perpetual motion running now the gauntlet of all-round criticism, but on only those truisms that do not need an additional experimental verification.

The thermokinetic approach to the body-of-mathematics construction is also different. It features using the whole arsenal of mathematical theorems covering a particular math model structure for the object under investigation (rather than "contriving" one's own means required for its investigation). Such an approach after N. Burbaki (1959) is called "structural-mathematical". It is based on the classic method of thermodynamic potentials, i.e. characteristic functions, the math operations on which define all properties of investigator's interest with regard to the object under investigation. This method is generalized to spatially heterogeneous systems by introducing, along with usual (thermodynamic) parameters such as temperature, pressure, volume, etc, also specific parameters of spatial heterogeneity. It rests on the properties of the exact differential of a number of non-equilibrium state functions and thus features quite general character. As for the rest of data describing the object under investigation, thermokinetics "imports" it "from outside" as uniqueness conditions of a kind when solving particular problems. Due to this all assumptions the investigator has made on the uniqueness conditions (hypotheses on substance structure, on molecular mechanism of processes, considerations on their properties correlation character, etc) do not touch the crux of the theory itself, i.e. the relations following from the math properties of characteristic functions. Such an approach makes it possible to keep the main advantage of the classic thermodynamic method and to lay it into foundation of a number of natural-science disciplines.

Chapter 1

METHODOLOGICAL PRINCIPLES OF THE THERMODYNAMICS

There are periods occurring now and then in the development of any natural-science theory when new ideas and experimental facts can not be crammed into "Procrustean bed" of its obsolete notional and conceptual system. Then the theory itself – its presuppositions, logical structure and body of mathematics – becomes the object of investigation. Thermodynamics went through such periods more than once (Gelfer, 1981). So was yet in the mid-XIX century when under the pressure of new experimental facts the concept of heat as an indestructible fluid collapsed and "entrained" (as seemed then) the S. Carnot's theory of heat engines (1824) based on it. A few decades later the threatening clouds piled up over the R. Clausius' mechanical theory of heat (1876) because of the "heat death of the Universe" – a conclusion deemed then as inevitable.

In the late XIX century great difficulties arose from attempts to conduct a thermodynamic analysis of composition variation in heterogeneous systems (at diffusion, chemical reactions, phase transitions, etc). J. Gibbs (1875) overcame the majority of those difficulties by representing closed system as a set of open subsystems (phases and components), which allowed him to reduce the internal processes of system composition variation to the external mass transfer processes. However, some of those difficulties have remained as yet and are showing, in particular, in the unsuccessful attempts to thermodynamically resolve the “Gibbs’ paradox” – a conclusion of stepwise entropy rise when mixing non-interacting gases and independence of these steps on the nature the gases feature and the degree they differ in (Chambadal, 1967; Kedrov, 1969; Gelfer, 1981; Bazarov, 1991).

During the XIX century thermodynamics also more than once encountered paradoxical situations that arose around it with the human experience outstepped. One of such situations arose with thermodynamics applied to the relativistic heat engines (contain fast moving heat wells) and showed in the statement that those could reach efficiency higher than in the Carnot’s reversible engine within the same temperature range (Ott, 1963; Arzelies, 1965; Meller, 1970; Krichevsky, 1970), as well as in the recognized ambiguity of relativistic transformations for a number of thermodynamic values (Bazarov, 1991). A little bit later a situation, not any less paradoxical, arose as connected with attempts to thermodynamically describe the systems of nuclear magnets (spin systems) with inverted population of energy levels. The negative absolute temperature concept introduced for such states led investigators to a conclusion of possibility for heat to completely convert into work in such systems and, on the contrary, impossibility for work to completely convert into heat, i.e. to the “inversion” of the principle fundamental for thermodynamics – excluded perpetuum mobile of the second kind (Ramsey, 1956; Abragam, 1958; Krichevsky, 1970, Bazarov, 1991).

That fate became common for also the theory of irreversible processes (TIP) created by extrapolating classic thermodynamics to non-equilibrium systems with irreversible (non-static) processes running therein. Problems arose primarily from the necessity to introduce into thermodynamics the transfer concepts inherently extraneous for it, from the incorrectness to apply the equations of equilibrium thermodynamics to irreversible processes in view of their inevitable change to inequalities, from the inapplicability of the classic notions of entropy and absolute temperature to thermally heterogeneous media, etc, which demanded to introduce a number of complimentary hypotheses and to attract from outside balance equations for mass, charge, momentum, energy and entropy with time involved as a physical parameter. Even heavier obstructions arise with attempts to generalize TIP to non-linear systems and states far away from equilibrium where the Onsager-Casimir reciprocal relations appear to be violated (S. Grot, 1956; R. Mason et al, 1972) and the law of entropy minimal production becomes invalid (I. Prigogine, 1960; I. Gyarmati, 1974). Attempts to overcome these difficulties without whatever correction on the conceptual fundamentals and body of mathematics of classic thermodynamics failed.

A remedy can be found in building of modern thermodynamics on its own more general notional and conceptual foundation with maximal care for the classic thermodynamic heritage.

1.1. Exclusion of Hypotheses and Postulates from Theory Grounds

One of the most attractive features of the thermodynamic method has always been the possibility to obtain a great number of consequences of various phenomena as based on few primary principles ("the beginnings"), which are empirical laws in their character for the thermo-mechanical systems. Being consistently phenomenological (i.e. empirical), that method enabled to reveal general behavior of various processes without intrusion into their molecular mechanism and resort to simulation of structure and composition of a system under investigation. Therefore, it is not by pure accident that all the greatest physicists and many mathematicians of the last century (Lorenz, Poincaré, Planck, Nernst, Caratheodory, Sommerfeld, Einstein, Born, Fermi, Neiman, Landau, Zeldovich, Feynman, etc) in their investigations placed high emphasis on thermodynamics and, based on it, have obtained many significant results.

However, thermodynamics have presently lost its peculiar position among other scientific disciplines. It sounds now in increasing frequency that thermodynamics relates to real processes to the same degree as Euclidean geometry to the Egyptian land surveyors' work. Such a standpoint is not groundless. Classic thermodynamics is known to have always done with two primary postulates taken for its "beginnings" – the laws of excluded "perpetuum mobile" of the first and second kinds. Those principles have had the exclusion character and empirical status. However, classic thermodynamics restricted to those two laws appeared to have been unable to solve the problems that arose with its extension to phenomena of another nature. So in consideration of open systems exchanging substance with the environment, the entropy absolute value and the substance internal energy had to be known. To know the values, the third "beginning" would be needed as stating their becoming zero at the absolute zero of temperature. In-depth analysis of the thermodynamic logic structure in works of C. Caratheodory (1907), T.A. Afanasjeva-Erenfest (1926), A.A. Guhman (1947, 1986) and their followers later led to the comprehension that the second law of thermodynamics would need to be split in two independent laws (existence and rise of entropy), as well as to realizing the important role of the equilibrium transitivity principle named the *zeroth law of thermodynamics* (Gelfer, 1981). Starting to study non-equilibrium systems with irreversible processes running therein additionally required the L. Onsager's reciprocity principle sometimes named the *fourth law of thermodynamics* from the phenomenological positions. Further investigations have revealed the fundamental difference between statistical thermodynamics and phenomenological thermodynamics and the fundamental role that plays for the latter the equilibrium self-non-disturbance principle, which has been assigned a part of its "general beginning" (I. Bazarov, 1991). Thus present day thermodynamics appears to be arisen from not two, but even seven beginnings! Meantime, the disputable consequences of thermodynamics are growing in number thus causing doubts in its impeccability as a theory. As R. Feynman wittily noted about this, "we have so many beautiful beginnings…but can't make ends meet nonetheless".

The law of excluded perpetuum mobile of the second kind being denied in open system thermodynamics (M. Mamontov, 1970), relativistic thermodynamics (H. Ott, 1963), spin system thermodynamics (M. Vukalovich, I. Novikov, 1968) excludes the possibility for thermokinetics to be based on the postulates of such a kind adopted for "the beginnings". The grave dissatisfaction investigators feel with such state of affairs has resulted in multiple attempts to build thermodynamics as based on other fundamental disciplines. This tendency has been most highlighted by A. Veinik (1968) in his *thermodynamics of real processes* based on a number of postulates of quantum-mechanical character, by M. Tribus (1970) in his *informational thermodynamics* based on the information theory formalism, and by C. Truesdall (1975) in his *rational thermodynamics* topology-based. All these theories feature a denial of the consistently phenomenological (i.e. based on only empirical facts) approach to the theory of irreversible processes, which deprives them of the basic advantage intrinsic for the classic thermodynamic method – the indisputable validity of its consequences.

In our opinion, one of the reasons of such a situation is that thermodynamics has lost its phenomenological nature with considerations of statistical-mechanical character gaining influence in its conceptual basis. Whereas the founders of statistical mechanics strived to lay the thermodynamic laws into the foundation of statistical theories, a statement has become now common that phenomenological thermodynamics itself needs a statistical-mechanical substantiation (despite "there are much ambiguity" in the grounds of the statistical theories (R. Cubo, 1970)). In particular, L. Onsager, the founder of the theory of irreversible processes (TIP), in order to substantiate the most fundamental concept of his theory – reciprocal relations, appealed to the principle of microscopic reversibility, the theory of fluctuations with a complementary postulate for linear character of their attenuation. All these statements evidently outspread beyond the thermodynamic applicability, therefore L. Onsager, not without reason, termed his theory *quasi-thermodynamics*.

Adoption of the *local equilibrium* hypothesis (I. Prigogine, 1947) for a basis of TIP construction became even "further-reaching" assumption. This hypothesis assumes (a) equilibrium in the elements of heterogeneous systems (despite the absence of the necessary equilibrium criterion therein – termination of whatever macro-processes); (b) possibility to describe their status with the same set of parameters as for equilibrium (despite the actual use of additional variables – thermodynamic forces) and (c) applicability of the basic equation of thermodynamics to these elements (despite its inevitable transformation into inequality in case of irreversible processes). As a result, the existing theory of irreversible processes does not reach the rigor and completeness intrinsic for the classic thermodynamic method.

Striving for excluding postulates from the grounds of thermokinetics dictates the necessity to base thermokinetics on only those statements that are beyond any doubt and construed as axioms. These statements include, in particular, the *equilibrium self-non-disturbance axiom* reading that a thermodynamic system once having reached equilibrium cannot spontaneously leave it. Unlike the equilibrium self-non-disturbance principle (general law of thermodynamics), this axiom does not claim that a thermodynamic system, being isolated, reaches equilibrium for a finite time. The axiom just reflects the evident fact that processes in a system that has reached equilibrium may be generated by only impact applied to it from outside and are, therefore, never observed in isolated systems. Being a result of the experience accrued, this axiom excludes the possibility the macro-physical state of a system will vary as a result of short-term spontaneous deviations from equilibrium (fluctuations) caused by the micro-motion of the constituent particles. Indeed, if fluctuations do not cause any variation in the microscopic (statistical in their nature) parameters of the system, they can not be considered as an energy-involving process since the energy of the system remains invariable. Here lies the fundamental difference between thermokinetics and statistical physics – the latter does consider fluctuations as the object of investigation. At the same time the equilibrium self-non-disturbance axiom allows for existence of systems that omit the equilibrium state in their development since this axiom does not claim for relaxation time finiteness, which is hardly provable.

The *process distinguishability axiom* is another primary statement thermokinetics appeals to. It states there are processes existing and definable (by all experimental means) which cause system state variations as specific, qualitatively distinguishable and irreducible to any other ones. In classic thermodynamics these are isothermal, isobaric, adiabatic, etc processes. It will be shown hereinafter that these two axioms, in conjunction with experimental data underlying the energy conservation, are enough to construct a theory both internally and externally consistent and generalizing thermodynamics to transfer processes and conversion of energy in any forms.

1.2. System Approach to Objects of Investigation

The deductive interpretation of classic thermodynamics (thermostatics) and the theory of non-static (irreversible) transfer processes as consequences from thermokinetics demands considering systems of a more general class as the object of its investigation. Classic thermodynamics is known to have been restricted to the investigation of intrinsically equilibrium (spatially homogeneous) systems wherein the intensive parameters such as temperature *T*, pressure *p*, chemical, electrical etc potentials were similar for all points of the system. It was dictated by not so much the simplicity of system description as by the necessity to keep the equations of thermodynamics from passing into inequalities with the spontaneous variations of system parameters. Thermodynamics of irreversible processes resting upon the local equilibrium hypothesis divided, with the same purpose, a system in whole heterogeneous into a number of homogeneous subsystems (down to elementary, supposedly equilibrium, volumes). The same is typical for the field theories such as continuum mechanics, hydrodynamics and electrodynamics, which also assume the continuum properties to be at that identical in whole to the properties of these elements and may be described in terms of relevant integrals. However, the extensive properties of heterogeneous systems are far from being always additive ones, i.e. the sum of properties of constituent elements. First of all, non-additive is the property of a heterogeneous system to do useful work as none of its local parts possesses it. It was S. Carnot who awoke to that statement in application to heat engines (1824) and put it into historically the first wording of the second law of thermodynamics. According to it, only thermally heterogeneous media possess a “vis viva (living force)”, i.e. are able to do useful work. In itself the notion of *perpetual motion of the second kind* as a system with no heat well and heat sink in its structure evidences the importance of considering such media as a single whole (but not as a set of thermally homogeneous elements). This is just the reason, why, at study of heat engines, the so-called “extended” systems have to be considered, which include, along with heat wells (sources), also heat sinks (receivers) (the environment).

Another non-additive property of heterogeneous media is the internal relaxation processes progressing and resulting, in absence of external constraint, in the equalization of densities, concentrations, electric charges, etc. among various parts of such a system. These processes are, however, absent in any element of the continuum considered as a locally equilibrium part of the system.

More non-additive properties are the *self-organization* ability of a number of systems, which is absent in any of their homogeneous part (S. Keplen, E. Essig, 1968; I. Prigogine, 1973,1986), as well as the *synergism* (collective action) phenomena appearing at only a definite hierarchic level of the system organization. The said refers in general to any structured systems, which specific features are determined by the inter-location and inter-orientation of the functionally detached elements and disappear with decomposition of the object of investigation into these elements (G. Gladyshev, 1988). Many of such elements (e.g., macromolecules and cells) being detached remain, however, spatially heterogeneous (locally non-equilibrium) despite their microscopic size (constituting *microcosmos* of a kind). This demands them being approached in the same way as the "extended" macro-systems.

For the further reasoning it is very important to show in the most general form that the main differential calculus technique – discretization of an object of investigation into infinity of homogeneous elementary volumes – results in the loss of *backbone* (system-forming) links. With this in mind let us consider the most general case of a system comprising the entire set of interacting material objects. Such a system is isolated by definition, while its internal energy U remains invariable with time t, i.e. $dU/dt = 0$. Let us represent this energy as the space integral $U = \int \rho_u dV$ of the energy density ρ_u. This gives for the system as a whole:

$$dU/dt = \int (\partial \rho_\varepsilon / \partial t) dV = 0. \qquad (1.2.1)$$

Integral (1.2.1) may be equal to zero with some processes available in a system if only the sign of the derivative $(\partial \rho_u / \partial t)$ is opposite in different areas of this system. This conclusion regards not only energy, but any other parameter obeying the law of conservation (mass, charge, momentum and angular momentum of the system), as well as the internal forces acting in such a system (as a closed one). From this it follows the *dichotomy law* as the major assertion for natural science in whole: processes running in isolated (closed) systems cause opposite variations of the properties in the different parts (areas) of such systems. That is why the set of interacting systems acquires new properties. From this it follows the main feature of the system approach, viz. the requirement to keep all backbone links undisturbed when investigating some part of a system, i.e. investigating the part through the whole (but not vice versa).

The system approach involves the binding consideration of *spatial heterogeneity* of the object under investigation. This becomes a necessary requirement for any theory pretending to be the one adequately explaining the reasons of processes running within whatever system. It is hardly necessary to prove the invalidity of the fundamental sciences to meet this requirement when they fraction systems into infinity of “elementary” areas, material points or particles supposed to be intrinsically equilibrium (homogeneous).

The such approach to objects of investigation dictates in itself the necessity of changing to consideration of spatially heterogeneous systems, which dichotomy (existing subsystems with opposite properties) is the reason of whatever processes arising therein. In line with this requirement the object of investigation by thermokinetics comprises spatially heterogeneous media considered as a *single non-equilibrium whole*. The size of such a system depends on the rate of its heterogeneity; therefore thermokinetics covers the broadest range of material objects – from nanoworld to megaworld – providing their properties can be successfully described with a finite number of state parameters. At the same time thermokinetics does not either exclude from consideration such a set of interacting bodies which may be considered, with acceptable accuracy, as a closed or isolated system. Thus, what was considered in thermodynamics as an “extended” system (including the environment besides the system itself), in thermokinetics becomes just a part of the system (subsystem) existing along with the similar other subsystems or with the object of work. In this case thermokinetics, from the very outset, has been consistent with the general scientific paradigm stating that any material object may not be deprived of its key property – extent, while any extended object – structure determined by its spatial heterogeneity.

1.3. Negation of Process and System Idealization outside the Framework of Uniqueness Conditions

Thermokinetics as a successive science needs to be extremely delicate to the classic thermodynamic inheritance. First of all this applies to the scope of the correctives introduced at that into the primary notions of thermodynamics. Let us dwell on those absolutely necessary in view of changing to consideration of systems of a broader class. Such a correction relates, in the first turn, to the notion of *process* as itself because of existing in heterogeneous systems a specific class of *stationary irreversible processes* wherein local parameters of a system as the object under investigation remain invariable despite the flows of heat, substance, charge, etc available in this system. Striving to keep the primary notion of "process" as a *succession of state variations* makes it necessary to define this notion as *any space-time variation of macro-physical properties pertaining to an object of investigation*. Thereby the state variations associated with the spatial transfer of various energy forms are included in the notion of process.

Changing to consideration of real processes also demands to negate the process idealization as implied in such notions as the *quasi-static, reversible, equilibrium*, etc process. The notion of *process* as a sequence of state variations of an object under investigation and the notion of *equilibrium* as a state featuring the termination of whatever processes are mutually exclusive. To eliminate this contradiction is to recognize that any non-static (running with a finite rate) process means equilibrium disturbance and is, therefore, irreversible. The acknowledgment of the fact that any non-static (running with finite rate) process involves the equilibrium disturbance and thus is irreversible was a turning point in the logical structure of thermodynamics. That demanded, as will be shown hereinafter, to negate the first law of thermodynamics as based on the energy balance equation and to seek for other ways to substantiate the law of energy conservation. Being though somewhat previous, we can note that the solution to that problem was found by construing energy as the function of state for a spatially heterogeneous system and through its representation in terms of the parameters of that state without respect to the character of the processes in the system. As a result, all the remainder information about an object under investigation including the equation of its state and the kinetic equations of the processes running therein may be successfully attributed to the uniqueness conditions that thermodynamics imports "from outside" when applied to solving particular problems. In thermodynamics so constructed all the assumptions an investigator imposes on the uniqueness conditions (including the hypotheses on matter structure and process molecular mechanism, which simplify the preconditions for the equations of state and laws of transfer) do not affect the core of the theory itself, viz. those relations which follow from the mathematical properties of energy and other characteristic functions of system state.

Such a construction of thermodynamics is advisably to be started off with a notion of *action* introduced into thermodynamics long before the law of energy conservation was discovered. The action in mechanics is construed as something that causes the momentum variation $Md\mathbf{v}_o$, where M – mass of the system, $\mathbf{v}_o$ – velocity of the mass center. According to the laws of mechanics the action value is expressed by the product of the force **F** and the duration of its action dt. This value is also called the *impulse of force*, N·s. A mechanical action is always associated with state variation, i.e. with process. Generalizing this notion to non-mechanical forms of motion the action will be construed as a *quantitative measure of a process associated with overcoming some forces*. The product of the action and the moving velocity $\mathbf{v} = d\mathbf{R}/dt$ of the object the force is applied to characterizes the amount of *work W*, J. The notion of work came to thermodynamics from mechanics (L. Carnot, 1783; J. Poncelet, 1826) where it was measured by the scalar product of the resultant force vector **F** and the induced displacement $d\boldsymbol{R}$ of the object it was applied to (radius vector **R** of the force application center)

$$đW = \mathbf{F} \cdot d\mathbf{R} \tag{1.3.1}$$

Thus work was considered as a quantitative measure of action from one body on another[1]. Later on forces were called mechanical, electrical, magnetic, chemical, nuclear, etc depending on their nature. We will denote the forces of the i^{th} kind by $\mathbf{F}_i$ – according to the nature of this particular interaction form carrier. Forces are additive values, i.e. summable over the mass elements dM, bulk elements dV, surface elements df, etc. This means that in the simplest case they are proportional to some factor of their additivity Θ_i (mass M, volume V, surface f, etc) and accordingly called *mass, bulk, surface,* etc *forces*. Forces are also subdivided into *internal* and *external* depending on whether they act between parts (particles) of the system or between the system and surrounding bodies (the environment).

However, when considering non-equilibrium and, in particular, spatially heterogeneous media, another property of forces takes on special significance, viz. availability or absence of their resultant **F**. To clarify what conditions this availability or absence, it should be taken into consideration that from the positions of mechanics the work some force does is the only measure of action from one body (particle) on another. The forces of the i^{th} kind generally act on the particles of different (the k^{th}) sort and hierarchical level of matter (nuclei, atoms, molecules, cells, their combinations, bodies, etc) possessing this form of interaction. Denoting the radius vectors of these elementary objects of force application by $\mathbf{r}_{ik}$ and the "elementary" force acting on them by $\mathbf{F}_{ik}$ gives that any i^{th} action on a system as a whole is added of elementary works

$$đW_{ik} = \mathbf{F}_{ik} \cdot d\mathbf{r}_{ik} \tag{1.3.2}$$

done on each of them ($đW_i = \Sigma_k \mathbf{F}_{ik} \cdot d\mathbf{r}_{ik} \neq 0$).

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[1] Note that according to the dominating scientific paradigm only the interaction (mutual action) of material objects exists so that work is the *most universal* measure of their action on each other.

The result of such action will evidently be different depending on the direction of the elementary forces $\mathbf{F}_{ik}$ and the displacements $d\mathbf{r}_{ik}$ they cause. Let us first consider the case when the elementary forces $\mathbf{F}_{ik}$ cause the like-sign displacement $d\mathbf{r}_{ik}$ of the objects of force application (particles of the k$^{\text{th}}$ sort), i.e. change the position of the radius vector $\mathbf{R}_i$ for the entire set of the k$^{\text{th}}$ objects the elementary forces $\mathbf{F}_{ik}$ are applied to. In such a case $d\mathbf{R}_i = \Sigma_k d\mathbf{r}_{ik} \neq 0$ and the forces $\mathbf{F}_{ik}$ acquire the resultant $\mathbf{F}_i = \Sigma_k \mathbf{F}_{ik}$. This is the work done by mechanical systems and technical devices (machines) intended for the purposeful energy conversion from one kind into another. Therefore in technical thermodynamics such a work is usually called *useful external* or *technical* (A.I. Andryushchenko, 1975, et al). However, since in the general case such a work is done by not only technical devices, but biological, astrophysical, etc systems as well, we will call it just the *ordered* work and denote by W^{e}. The work of the i$^{\text{th}}$ kind is defined as the product of the resultant $\mathbf{F}_i$ and the displacement $d\mathbf{R}_i$ it causes on the object of its application:

$$đW_i^{\text{e}} = \mathbf{F}_i \cdot d\mathbf{R}_i \,. \qquad (1.3.3)$$

In Chapter 3 we will make certain that this work definition is universal. The ordered work process features its *vector character*.

The work done at the uniform compression or expansion of a gas with no pressure gradients ∇p therein is another kind of work. Considering the local pressure p as a mechanical force acting on the vector element of the closed surface df in the direction of the normal and applying the gradient theorem to the pressure forces resultant $\mathbf{F}_p$, gives:

$$\mathbf{F}_p = \int p df = \int \nabla p \; dV \; = 0. \qquad (1.3.4)$$

Thus the uniform compression work on an equilibrium (spatially homogeneous) system is not associated with the pressure forces resultant to be overcome, while the compression or expansion process itself is not associated with changing the position of the body as a whole. From the standpoint of mechanics where work has always been understood as an exclusively quantitative measure of energy conversion from one form into another (e.g., kinetic energy into potential one) this means that at the uniform compression the energy *conversion* process itself is absent. Due to the absence of the ordered motion of the i^{th} object (its displacements $d\mathbf{R}_i = 0$) the work of such a kind will be hereinafter called *unordered* and denoted by $W^{\text{н}}$. This category should also include many other kinds of work not having a resultant, in particular, the work of uniformly introducing the k^{th} substances (particles) or charge into the system, imparting relative motion momentum to the system components, etc. This category should further include heat exchange that is nothing but "micro-work" against chaotic intermolecular forces. As will be made certain hereinafter, the absolute value of the specific unordered forces F_i/Θ_i is construed as the *generalized potential* Ψ_i (absolute temperature T, pressure p, electrical φ, chemical μ_k potential of the kth substances, etc). Thus the unordered work is done against forces not having a resultant. Therefore the unordered work process features the scalar character characterizing the transfer of energy in the same form (without energy conversion). This is the situation we encounter at the equilibrium heat or mass exchange and uniform cubic strain.

The work of dissipative character W^d constitutes a special work category. This work is done by the ordered forces $\mathbf{F}_i$ against the so-called *dissipative forces* not having a resultant because of their chaotic directivity. Therefore the dissipative work features a mixed (scalar-vector) character, i.e. is associated with changing from *ordered* forms of energy to *unordered* ones.

Fig. 1.1 illustrated a work classification based on the force difference. energy conversion available in the ordered work processes is here indicated by superseding the subscript i by the subscript j = 1, 2, …, n according to the nature of the forces being overcome. External work done (against environmental forces) is denoted by the superscript *env*. This work involves transferring a part of energy in a modified form to other bodies (environment). Internal work keeps the energy of the system invariable and involves its conversion from one form into another (as it occurs in oscillation processes or cyclic chemical reactions of Belousov-Zhabotinsky's type). Hereinafter this classification will underlie the classification of energy by its forms.

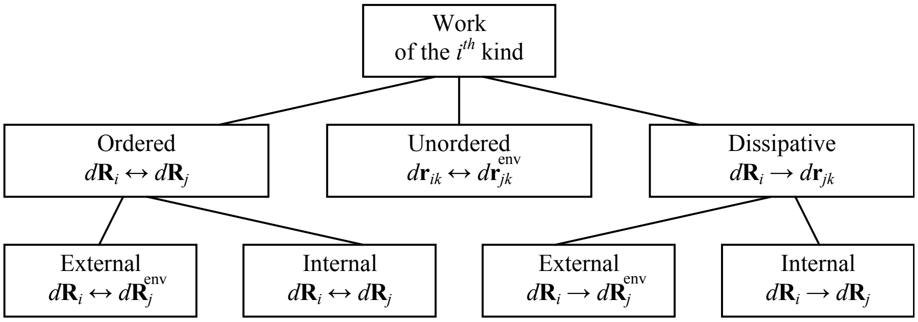

Fig.1.1. Work Classification for Non-Equilibrium Systems

The term *heat* in the present-day technical literature is used in two meanings: as a *state* function (called briefly the *body heat*) and as a *process* function serving as a *quantitative measure of heat exchange* (and called briefly the *process heat*)[1]. This duality in construing heat appeared historically with considering heat as a chaotic form of motion (amongst such phenomena as light, sound, electricity, magnetism) and has remained notwithstanding multiple discussions. The conception of heat as a form of energy has been reflected in the notion of heat capacity of system. It has as well strengthened its position in the heat exchange theory (to the principle: a system can exchange only what it has). In non-equilibrium systems such an understanding of heat is dictated by a number of thermal effects caused by dissipation (friction, diathermic or induction heating, chemical transformations, etc). These heats are not supplied from outside either, though relate to *process*. However, in equilibrium systems of such a kind thermal effects are absent and heat becomes just a quantitative measure of heat exchange process. Therefore in equilibrium thermodynamics heat is often interpreted as the energy being transited from one body to another, i.e. something that is supplied from outside across the system borders, but not contained in the system itself.

Accepting the said duality for objectivity we will take into consideration both the body heat and the process heat denoting the former by U_B (to avoid mishmash), while the latter – by Q and applying the exact differential sign d for infinitesimal increments of any state function (including U_B), while the inexact differential $đ$ – for the elementary heat amounts $đQ$ as process functions (C. Neuman, 1875). The same inexact differential sign will be applied for also the work $đW$ when it becomes dependent on the process path (i.e. becomes process function).

A specific kind of the energy exchange existing in the general case of open systems and associated with the substance (mass) exchange compels us to completely refuse the classic division of the energy exchange in such systems into *heat exchange* and *work*. The point is that putting substance into material medium always involves the so-called “input work” and the interchange of internal heat energy (body heat) between bodies. Therefore the notions of heat and work lose their sense “on the border where substance diffusion takes place” (M. Tribus, 1970).

The impossibility to reduce the process heat to only “one of the forms of energy exchange” (K. Putilov, 1971), as well as the existence of only one kind of energy exchange (mass exchange) in open systems forces absolutely rejecting the classic division of energy exchange into *heat* and *work* in non-equilibrium systems. The fundamental difference between the *ordered* and *unordered* work in non-equilibrium systems being perceived, heat exchange needs to be ascribed to the category of unordered work (against forces not having a resultant like the work of dissipative character). Interpreting the

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[1] Thermodynamics. Terminology // under the editorship of I.I. Novikov. M.: AN USSR, 1973. Edition 85

heat exchange as some *micro-work* against intermolecular forces directed in random way means the above notions are realized as different in their scale, while work is realized as a unitary quantitative measure of action from some material objects on other ones.

The abovementioned order of concepts clarifies the meaning and position of the notion of *energy*. The term *energy* (from Greek *activity*) was introduced into mechanics in the early XIX century by T. Young, an authoritative physicist, as a substitution for the notion of *living force* and meant the work which a system of bodies could do when decelerating or going over from a particular configuration into the "zeroth" one (adopted for the base). The energy was accordingly divided into kinetic $E^к$ и потенциальную $E^р$. The term *potential* meant that the energy could be realized in the form of work only with appearing the relative motion of interacting bodies, i.e. with changing their mutual position. The sum of kinetic and potential energies in an isolated (closed) system did not remain constant because of a known phenomenon of energy *dissipation* caused by unordered work done against the dissipation (friction) forces. Because of dissipation the real systems (with friction) spontaneously lost their capacity for external work. That meant the only thing, viz. the transition of energy as a microscopically ordered form of motion into the latent (microscopic) form of motion (interaction). Later, with thermodynamics appeared, that standpoint was supported by proving the internal energy U as inherent to bodies. That allowed stating the law of conservation of total energy that was construed as the sum of kinetic $E^к$, potential $E^р$ and internal U energies of an isolated system:

$$(E^к + E^р + U)_{\text{isol}} = \text{const}. \tag{1.3.5}$$

However, in that case the notion of energy lost its primary sense of the capacity for external work as ensued from the word-group etymology of Greek εν (en) for *external* and εργον (ergon) for *action*. Indeed, according to the second law of thermodynamics the internal energy U can not be entirely converted into work. For this reason the energy of real systems ceased to be determined by the amount of useful work done. And the work itself ceased to be the exact differential since became dependant on the process path and rate (dissipation conditioning), but not on exclusively the initial and final states of the system. To simplify the situation, mechanics was supplemented with a provisional notion of *conservative* system, where the sum of kinetic and potential energies could be considered as a value kept and dependant on exclusively the initial and final states of the system. However, in that case all the consequences of mechanics as having ensued from the energy conservation law were naturally restricted to only the conservative systems.

That engendered some ambiguity in the notion of energy, which has not yet been resolved. A reader is usually very surprised with not finding in physical guides and encyclopedia a definition of this notion more substantial than the philosophic category of *general quantitative measure of all kinds of matter*. As H. Poincaré bitterly noted, “we can say of energy nothing more but that something exists remaining invariable”. Regarding the value that brings together all phenomena of the surrounding world such a definition is absolutely insufficient, the more so because not only energy remains invariable in isolated systems, but also mass, momentum, charge and angular momentum!

The definition thermokinetics offers for work through action and work interpreted as the only quantitative measure of action from some bodies on other ones allows returning to energy its simple and clear meaning as the capacity of a system to do work. However, now energy becomes a quantitative measure of all (ordered and unordered, external and internal, useful and dissipative) works a system can do. This approximates to the J. Maxwell’s definition of energy as the “sum of all effects a system can have on the surrounding bodies”. Next chapters will be dedicated to the substantiation of formal consistency and advisability of such an approach.

1.4. Number-of-Degrees-of-Freedom Theorem as a Basis of Real Processes Classification

Changing over to non-equilibrium systems with spontaneous processes running therein needs to generalize the thermodynamic principle of *process classification* itself. The point is that the same state variations (e.g., heating of a body) in spatially heterogeneous systems may be caused by both the external heat exchange and appearing internal friction heat sources, chemical reactions, diathermic heating, magnetization reversal, etc. In the same way the cubic strain of a system can be induced by not only the compression work, but a spontaneous expansion into void as well. Hence processes in thermokinetics should be classified regardless of what causes whatever state variations – the external heat exchange or internal (including relaxation) processes.

In this respect thermokinetics differs from both physical kinetics that classifies processes by reasons causing them (distinguishing, in particular, concentration diffusion, thermal diffusion and pressure diffusion) and the heat exchange theory that distinguishes processes by the mechanism of energy transfer (conductive, convective and radiant). Processes in thermokinetics will be classified by their *consequences, i.e. by special state variations they cause as phenomenologically distinguishable and irreducible to others*. We will call such processes, for short, *independent*. These include, in particular, isochoric, isobaric, isothermal and adiabatic processes thermal physics considers. Here comes the *heat process* as well (K. Putilov, 1971), which we will construe as a variation of the body internal thermal energy U_B regardless of what causes it – either heat exchange or internal heat sources. Other processes are also included, e.g., the system composition variation process that may be caused both by substance diffusion across the system borders and chemical reactions inside the system.

With the principle of process classification adopted as based on distinguishability of processes specific demands are made on choosing their "coordinate", i.e. a *physical value which variation is the necessary and sufficient criterion of running a particular process*. These demands consist in choosing only such a parameter as the process coordinate that *does not vary*, when other, also independent, processes are simultaneously running in the same space points. It is that approach wherefrom the requirement in classic thermodynamics follows for the invariability of entropy as the heat exchange coordinate in adiabatic processes as well as the requirement itself for the process reversibility, i.e. the absence of spontaneous entropy variations not connected with the external heat exchange.

The principle of classification of real processes by their consequences and the axiom of their distinguishability enable substantiating a quite evident though fundamental statement stipulating that *the number of independent coordinates conditioning the state of any (either equilibrium or non-equilibrium) thermokinetic system equals the number of degrees of its freedom, i.e. the number of independent processes running in the system*.

This statement (or theorem) is easily provable "by contradiction". Since a thermodynamic process is construed as variation of the properties of a system expressed in terms of state parameters, at least one of such parameters necessarily varies when processes are running. Let's assume that several state parameters necessarily vary when some independent process is running. Then these parameters will not evidently be independent, which violates the primary premise. Now let's assume that some coordinate of the system necessarily varies when several processes are running. Then these processes will not evidently be independent since they cause the same variations of the system properties – the fact that also violates the primary premise. We have nothing to do, but to conclude that *only one independent state coordinate corresponds to any* (equilibrium or non-equilibrium, quasi-static or non-static) *independent process*. Such coordinates are generally extensive variables since each of them defines, in the absence of other degrees of freedom, the energy of a system, which is an extensive value as well.

The proven statement defines the *necessary and sufficient* conditions for unique (deterministic) definition of state for whatever system. Therefore, it may be, for ease of reference, reasonably called the state *determinacy principle*. This principle makes it possible to avoid both the "under-determination" and "over-determination" of a system[1] as the main cause of the methodological errors and paradoxes of present-day thermodynamics (V. Etkin, 1979, 1991). The continuum state "under-determination" as resulting from the local equilibrium hypothesis adopted is, e.g., far from evidence. This hypothesis excludes the necessity of the gradients of temperature, pressure and other generalized potentials (i.e. thermodynamic forces) in the fundamental equation of non-equilibrium thermodynamics on the ground that the bulk elements are assumed to be equilibrium. On the other hand, the continuum "over-determination" due to the infinite number of degrees of freedom ascribed to it despite the finite number of macro-processes running therein is either not evident.

The theorem proven allows, in its turn, to concretize the notion of system *thermokinetic state*, which is construed as a set of only such properties that are characterized by the set of state coordinates strictly defined in their number. This means that such system properties as color, taste, smell, etc, which are not characterized by state parameters quantitatively and qualitatively may not be considered as thermodynamic. This relates, in particular, to also the "rhinal", "haptic", etc number of freedom A. Veinik arbitrarily introduced (1968) for a system.

One of the consequences of the determinacy principle consists in the necessity to introduce additional state coordinates for systems where, along with external heat exchange processes, internal (relaxation) processes are observed as tending to approximate the system to the equilibrium state. Without such variables introduced it is impossible to construct a theory covering the entire spectrum of real processes – from quasi-reversible up to critically irreversible.

1.5. Extension of Variables Space with Introduction of Spatial Heterogeneity Parameters for System as a Whole

The fact that relaxation vector processes (temperature, pressure, concentration, etc equalization) run in non-equilibrium systems requires introducing specific parameters of spatial heterogeneity characterizing the state of continuums as a whole. To do so, it is necessary, however, to find a way how to change over from the density (fields) distribution functions

$$\rho_i = d\Theta_i/dV$$

of some extensive physical values Θ_i to the parameters of the system as a whole, which thermodynamics operates with. This change may be

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[1] I.e. the attempts to describe the system state by a deficient or excessive number of coordinates.

conducted in the same way as used in mechanics to change over from motion of separate points to system center-of-mass motion. To better understand such a change, let us consider an arbitrary continuum featuring non-uniform density distribution $\rho_i = \rho_i(\mathbf{r},\mathrm{t})$ of energy carriers1) over the system volume V. Fig.1.2 illustrates the arbitrary density distribution $\rho_i(\mathbf{r},\mathrm{t})$ as a function of spatial coordinates (the radius vector of a field point $\mathbf{r}$) and time t. As may be seen from the figure, when the distribution Θ_i deviates from that uniform (horizontal line), some amount of this value (asterisked) migrates from one part of the system to other, which displaces the center of this value from the initial $\mathbf{R}_{i0}$ to a current position $\mathbf{R}_i$.

Position of the center of a particular extensive value Θ_i defined by the radius vector $\mathbf{R}_i$ is given by a known expression:

$$\mathbf{R}_i = \Theta_i^{-1} \int \rho_i(\mathbf{r},t)\, \mathbf{r}\mathrm{dV}\ , \ (i = 1,2,\ldots,\mathrm{n}) \qquad (1.5.1)$$

For the same system, but in a homogeneous state, the Θ_i center position $\mathbf{R}_{i0}$ may be derived if factoring $\rho_i = \rho_{i0}(\mathrm{t})$ in equation (2.1.1) outside the integral sign:

$$\mathbf{R}_{i0} = \Theta_i^{-1} \int_{\mathrm{V}} \rho_{i0}\left(t\right)\mathbf{r}\mathrm{d}V = V^{-1} \int_{\mathrm{V}} \mathbf{r}\mathrm{d}V. \qquad (1.5.2)$$

Thus the state of a heterogeneous system features the emergence of specific "distribution moments" $\mathbf{Z}_i$ of the energy carriers Θ_i:

$$\mathbf{Z}_i = \Theta_i(\mathbf{R}_i - \mathbf{R}_{i0}) = = \int_V \left[\rho_i(\mathbf{r},t) - \rho_{i0}(t)\right]\mathbf{r}dV. \qquad (1.5.3)$$

The electrical displacement vector $\mathbf{D} = \Theta_\mathrm{e}\Delta\mathbf{R}_\mathrm{e}$ is one of such moments with Θ_e as electrical charge and $\Delta\mathbf{R}_\mathrm{e}$ as displacement of its center.

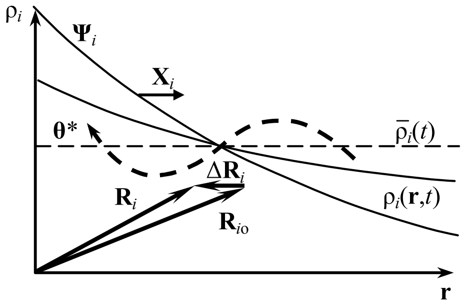

Fig.1.2. To Generation of Distribution Moment

Expression (1.5.3) most evidently manifests that the parameters $\mathbf{Z}_i$ of spatial heterogeneity are additive values and summed up providing the $\rho_{i0}(t)$ value remains the same in various parts of a heterogeneous system.

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1) The Energy carrier is construed as a material carrier of the i^{th} Energy component, which quantitative measure is the physical value Θ_i. So the mass $\mathrm{M_k}$ of the k^{th} substance is a carrier of the rest Energy; the charge Θ_e – a carrier of the electrostatic Energy of the system; the component momentum $\mathrm{M_k v_k}$ – a carrier of its kinetic Energy, etc.

This follows from the conservation of integral (1.5.3) at its partition into parts with a volume $V' < V$[1]. However, these parameters become zero at "contraction" of the system to a material point, when $\rho_i(\mathbf{r},t) \rightarrow \rho_{i0}(t)$. This stands in absolute conformity with the degrees-of-freedom theorem because the processes of density redistribution $\rho_i(\mathbf{r},t)$ are absent in material points. And once again this confirms the fact that an entity of continuum elements considered as a system, non-equilibrium in whole, possesses additional degrees of freedom.

For any part of a homogeneous isolated system the $\mathbf{R}_{i0}$ value remains unvaried since running of any processes is herein impossible. Therefore the $\mathbf{R}_{i0}$ may be accepted for such systems as a reference point $\mathbf{r}$ or $\mathbf{r}_i$ and set equal zero ($\mathbf{R}_{i0} = 0$). In this case the vector $\mathbf{R}_i$ will define a displacement of the Θ_i center from its position for the system being in internal equilibrium state, and the moment of distribution of a particular value Θ_i in it will become:

$$\mathbf{Z}_i = \Theta_i \mathbf{R}_i \tag{1.5.4}$$

Herein the moment $\mathbf{Z}_i$ becomes an absolute extensive measure of the system heterogeneity with respect to one of the system properties – like such absolute parameters of classic thermodynamics as mass, volume, entropy, etc.

As follows from expressions (1.5.2) and (1.5.3), the distribution moment $\mathbf{Z}_i$ emerges due to exclusively the displacement of the Θ_i center and has nothing to do with the variation of this value itself. Thus the expression for the exact differential of the function $\mathbf{Z}_i = \mathbf{Z}_i(\Theta_i,\mathbf{R}_i)$ becomes:

$$d\mathbf{Z}_i = (\partial \mathbf{Z}_i/\partial \Theta_i)\mathrm{d}\Theta_i + (\partial \mathbf{Z}_i/\partial \mathbf{R}_i)d\mathbf{R}_i\,, \tag{1.5.5}$$

resulting in:

$$\Theta_i = \nabla\cdot\mathbf{Z}_i \ \text{ and } \ \rho_i = \nabla\cdot\mathbf{Z}_{iV}\,, \tag{1.5.6}$$

where $\mathbf{Z}_{iV} = \partial \mathbf{Z}_i/\partial V$ – distribution moment in the system unit volume.

In case of discrete systems the integration over system volume will be replaced by the summation with respect to elements $d\Theta_i$ of the Θ_i value:

$$\mathbf{Z}_i = \Theta_i \mathbf{R}_i = \Sigma_i\, \mathbf{r}_i\, \mathrm{d}\Theta_i\,, \tag{1.5.7}$$

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[1] With symmetrical density $\rho_i(\mathbf{r},t)$ distributions for whatever parameter, e.g., fluid-velocity profiles in tubes, expression (1.5.3) should be integrated with respect to annular, spherical, etc layers with $V' > 0$, wherein the function $\rho_i(\mathbf{r},t)$ is monotone increasing or decreasing.

where $\mathbf{r}_i$ – radius vector of the element $d\Theta_i$ center. Therefore expressions (1.5.4) through (1.5.6) remain valid for also the systems with discrete distribution of charges, poles, elementary particles, etc. Only the geometrical meaning of the $\Delta\mathbf{R}_i$ vector changes; for symmetrical distributions the vector is defined by the sum of the displacements $\Delta\mathbf{r}_i$ of all elements $d\Theta_i$. This may be instantiated by the centrifugal "shrinkage" of the particles' momentum flow in moving liquid when forming turbulent or laminar fluid-velocity profiles in channels ("boundary layer" formation and build-up).

Explicitly taking into account the spatial heterogeneity of systems under investigation is decisive in further generalization of the thermodynamic investigation method to non-equilibrium systems. As a matter of fact, this is the spatial heterogeneity (heterogeneity of properties) of natural objects that causes various processes running in them. This implies the exclusive role the distribution moments $\mathbf{Z}_i$ play as a measure for deviation of a system in whole from internal equilibrium of the i^{th} kind. Introducing such parameters allows precluding the major drawback of non-equilibrium thermodynamics, viz. lack of extensive variables relating to the gradients of temperature, pressure, etc. Classic thermodynamics is known to have crystallized into an independent discipline after R. Clausius succeeded in finding a coordinate (entropy) related to temperature in the same way as pressure to volume and thus determinately described the simplest thermo-mechanical systems. The distribution moments $\mathbf{Z}_i$ play the same part in thermokinetics coming into being. As will be shown later, these relate to the main parameters introduced by non-equilibrium thermodynamics – thermodynamic forces, in the same way as the generalized potentials to the coordinates in equilibrium thermodynamics. These are the distribution moments which make the description of heterogeneous media a deterministic one thus enabling introducing in natural way the concept of generalized velocity of some process (flow) as their time derivatives. They visualize such parameters as the electrical displacement vectors in electrodynamics and generalize them to phenomena of other physical nature. In mechanics the $\mathbf{Z}_i$ parameters have the dimension of action (Θ_i – momentum of a body, $\mathbf{R}_i$ – its displacement from equilibrium position), imparting physical meaning to this notion. These are the parameters which allow giving the analytic expression to the system working capacity having thus defined the notion of system energy. Using such parameters provides a clear view of the degree of system energy order, enables proposing a universal criterion of the non-equilibrium system evolution, etc. Paraphrasing a M. Planck's statement regarding entropy one may positively say that the distribution moments are exactly the parameters entire non-equilibrium thermodynamics is "standing and falling" with.

1.6. Coordinates of Non-Equilibrium Redistribution and Reorientation Processes

The moments of distribution (1.5.5) contain vectors of displacement $\mathbf{R}_i$, each of which can be expressed product of a basic (individual) vector $\mathbf{e}_i$, characterising its direction, on module $R_i = |\mathbf{R}_i|$ this vector. Therefore the complete variation of the displacement vector $\mathbf{R}_i$ may be expressed as the sum of two summands:

$$d\mathbf{R}_i = \mathbf{e}_i d\mathrm{R}_i + \mathrm{R}_i d\mathbf{e}_i\,, \tag{1.6.1}$$

where the augend $\mathbf{e}_i d\mathrm{R}_i = d\mathbf{S}$ characterizes elongation of the vector $\mathbf{R}_i$, while the addend $\mathrm{R}_i d\mathbf{e}_i$ – its turn.

Let us express now the $d\mathbf{e}_i$ value characterizing the variation of the distribution moment direction in terms of an angular displacement vector $\boldsymbol{\varphi}$ normal to the plane of rotation formed by the vectors $\mathbf{e}_i$ and $d\mathbf{e}_i$. Then the $d\mathbf{e}_i$ will be defined by the external product $d\boldsymbol{\varphi}_i \times \mathbf{e}_i$ of vectors $d\boldsymbol{\varphi}_i$ and $\mathbf{e}_i$, so the addend in (1.6.1) will be $\Theta_i R_i d\mathbf{e}_i = d\boldsymbol{\varphi}_i \times \mathbf{Z}_i$. Hence, expression of full differential of the distribution moments looks like:

$$d\mathbf{Z}_i = (\partial\mathbf{Z}_i/\partial\Theta_i)d\Theta_i + (\partial\mathbf{Z}_i/\partial\mathbf{S}_i)d\mathbf{S}_i + (\partial\mathbf{Z}_i/\partial\boldsymbol{\varphi}_i)d\boldsymbol{\varphi}_i. \tag{1.6.2}$$

According to the degrees-of-freedom theorem this means that any state function describing a heterogeneous system in whole are generally defined by also the full set of variables Θ_i, $\mathbf{S}_i$ and $\boldsymbol{\varphi}_i$. Since further resolution of the vector $\mathbf{Z}_i$ is impossible, expression (1.5.5) indicates there are three categories of processes running in heterogeneous media, each having its own group of independent variables. The first-category processes running at $\mathbf{R}_i$ = const involve the uniform variation of the physical value Θ_i in all parts of the system. Such processes resemble the uniform rainfall onto an irregular (in the general case) surface. Here comes, in particular, the pressure field altered in liquid column with variation of free-surface pressure. These processes also cover phase transitions in emulsions, homogeneous chemical reactions, nuclear transformations and the similar scalar processes providing the composition variations they induce are the same in all parts of the system. We will call them hereinafter the *uniform processes* regardless of what causes the increase or decrease in amount of whatever energy carrier Θ_i (and the momentum associated) – either the external energy exchange or internal relaxation phenomena. These processes comprise, as a particular case, the reversible (equilibrium) processes of heat exchange, mass exchange, cubic strain, etc, which, due to their quasi-static nature, practically do not disturb the system spatial homogeneity.

Processes described by the addend in (1.5.5) run with the Θ_i parameters being constant and consist in their redistribution among the parts (zones) of a heterogeneous system. They involve decreasing, e.g., the entropy S', mass M', its momentum $\mathbf{P}'$, its volume V', etc, in some parts of the system and by increasing the same in other parts. Such processes are associated with the Θ_i value center position variation $\mathbf{R}_i$ within the system and resemble the migration of fluids from one part of a vessel into another. Therefore we will call them the *redistribution* processes. Such processes are always non-equilibrium even if they run infinitely slowly (quasi-statically) since the system remains spatially heterogeneous in this case. State modifications of such a kind are caused by, e.g., the useful external work of external forces, the non-equilibrium energy exchange processes that induce non-uniform variation of the Θ_i coordinates inside the system, and the vector relaxation processes involving equalization of temperature, pressure, chemical and other system potentials. All processes of such a kind feature a directional (ordered) character, which distinguishes the useful work from the work of uniform (quasi-static) introduction of substance, charge, etc, or the expansion work. According to (1.3.2) the coordinates of the processes pertaining to this category are understood as the displacement vectors $\mathbf{S}_i$. These coordinates should be attributed to the *external parameters* of the system since they characterize the *position* of the energy carrier Θ_i center in whole relative to external bodies (the environment) just as the center of mass $\mathbf{S}_m$ of the system or its center of inertia $\mathbf{S}_w$.

There are also the processes of *reorientation* of magnetic domains, electrical and magnetic dipoles, axes of rotation of bodies, etc., running in a number of systems, e.g., in ferromagnetic materials. The micro-world manifests them in, e.g., the unified spin-orientation arrangement' the macro-systems – in the spontaneous magnetization of ferromagnetic materials, while the mega-world – in the close-to-equatorial plane alignment of the galaxies' spirals, asteroidal belts, orbits of the primary planets and their satellites, etc. The systems with processes of such a kind will hereafter be called, for short, *oriented*. These include also the bodies with shape anisotropy. The reorientation processes are not reducible to the transfer and redistribution processes either. This means that the coordinate of such kind a process is a variation of the angle $\boldsymbol{\varphi}_i$ characterizing the orientation of distribution moment $\mathbf{Z}_i$ of the system as a whole.

Thus, all processes running in heterogeneous systems may be broken down into three groups: *uniform, redistribution* and *reorientation processes*, which coordinates are, respectively, variables Θ_i, $\mathbf{S}_i$ and $\boldsymbol{\varphi}_i$. This fundamentally distinguishes thermokinetics from classic thermodynamics and the theory of irreversible processes, where the state of a system is defined by exclusively a set of thermostatic variables Θ_i.

The undertaken expansion of the space of variables by introducing the vectors of displacement $\mathbf{R}_i$ makes it possible to cover not only quantitative, but as well *qualitative* variations of energy in various forms. The fact that *vector processes* run in systems along with *scalar processes* means that both the *ordered* W^e and *unordered* W^{un} works are generally done in such systems. It becomes clear that the irreversibility of real processes associated with the energy dissipation (i.e. with losing the capacity for ordered work) becomes apparent in the process *scalarization*, i.e. in losing vector character of the process. Furthermore, a possibility appears to further distinguish between the *energy transfer* processes (i.e. the energy transfer between bodies in the same form) and the *energy conversion* processes (i.e. the energy conversion from one form into another)[1].

This is enough in principle to construct a unitary theory of real processes enabling investigation of any systems (simplex and complex, closed and open, homogeneous and heterogeneous, isolated and non-isolated, tending to and omitting equilibrium) not outstepping the strict applicability of its primary concepts.

Chapter 2

Specificity of Thermokinetics in Application to Spatially Heterogeneous Systems

As the practice shows, studying a scientific discipline, especially acquiring it inasmuch as necessary for an independent activity is most successful if a reader is from the very first introduced to a critical presentation of the existing situation, to fundamentals of the discipline and general methods of solving particular problems. Therefore in this chapter we will review, along with a historical synopsis, specific features of thermokinetics allowing it to apply its body of mathematics to any systems – simplex and complex, closed and open, homogeneous and heterogeneous, tending to and omitting equilibrium in their development.

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[1] As will be shown hereinafter, the Energy transfer is associated with unordered work done, whereas the Energy conversion – with ordered work.

2.1. Substantiation of Total energy Conservation Law

Classic thermodynamics is known to be based on the principle of heat Q and work W equivalence. R. Clausius, the founder of classic thermodynamics, formulated this principle as follows, ”In all cases, when heat becomes work in a cyclic process, the amount of the heat expended is proportional to the work done and vice versa, work done is converted into an equivalent amount of heat” (Clausius, 1876). If heat and work are measured in the same units of the international system of units, SI, the equivalence principle may be written as a simple relationship:

$$W_c / Q_c = \oint đW / \oint đQ = 1, \qquad (2.1.1)$$

где W_c, Q_c – work done and heat supplied for cycle; $đW$, $đQ$ – their elementary amounts for particular parts of the cyclic process under consideration.

Taking into consideration the rule of signs accepted in thermodynamics (the work done by a system and the heat supplied to it are positive) equation (2.1.1) becomes:

$$\oint (đQ - đW) = 0. \qquad (2.1.2)$$

Clausius was the first who noticed that the above result did not depend on the path of the process under consideration. That allowed him to use a known mathematical theorem of curvilinear integrals. It states that if a curvilinear integral of an arbitrary differential form (in our case $đQ - đW$) becomes zero along any closed path within some space of variables, the integrand represents the exact differential of function of these variables U:

$$dU = đQ - đW \text{ or } đQ = dU + đW. \qquad (2.1.3)$$

R. Clausius did not concretize the space of variables wherein he considered the curvilinear integral (2.1.2) since he had not yet found the heat exchange (entropy) coordinate. Therefore he initially called the function U the *total heat of a body* having construed it as the sum of the heat the body received from outside and the heat released as a result of the *disgregation work* (of dissipative character). That caused some confusion in notions since imparted the status of state function to heat and disgregation work. Therefore a rather heated discussion combusted about the U function. In particular, W. Thomson recommended the term *mechanical energy of a body in particular state* for the U value. From that time on this function has been referred to as the *internal energy*. Being the state function of a system, that function did not depend on the motion or position of the system relative to the environment. In such a case the isolation of the system from the environment (Q, $W = 0$) left that function invariable. Based on that fact, expression (2.1.3) started to be considered in classic thermodynamics as a particular case of the *energy conservation law* called the first law of thermodynamics.

Since classic thermodynamics from its origin has always been restricted to describing the behavior of internally equilibrium (spatially homogeneous) systems with parameters the same for all of the system parts, all kinds of work such a system could do had the *unordered* character (see Chapter 1). Here comes, in particular, the uniform compression work $\text{đ}W_p$ expressed through the product of the absolute pressure p and the volume variation dV. In such a case the U function could actually be construed as the dissipated part of energy, which corresponded to the law of energy conservation in the form of (1.3.4). However, in the more general case of non-equilibrium and especially spatially heterogeneous systems this is far from being so. In particular, the chemical and nuclear energy of homogeneous systems is also partly convertible into other forms despite they do not either depend on the position of the system relative to surrounding bodies, i.e. relate to internal energy. The situation became even more complicated with changing to the spatially heterogeneous systems to be studied, in particular, to the so-called *extended* systems with the environment included. Such systems can do some useful work before internal equilibrium has set in there. These systems may comprise also polarized and magnetized bodies located in external force fields. In all those cases the internal energy U ceased being that "dissipated" part of energy meant in (1.3.4).

All this impels to search for a more general substantiation of the law of its conservation. To this end let us consider the results of those experiments on definition of the heat and work equivalence principle, which related to non-equivalent systems with relaxation processes running therein. Their specific character was such that heat was obtained there by friction (dissipation). These include classic experiments by Joule, in particular, the experiment with calorimeter and agitator driven by dropping weight; also his experiment with the Proney brake that brakes the drum calorimeter (1843-1878); Girn's experiments with lead flattening on anvil with drop hammer (1859); Lenz's experiments with solenoid discharging to active resistance in vessel calorimeter (1972) and many other experiments involving battery charging, gas transfer between vessels, electrolyte decomposition, etc (J. Gelfer, 1969,1973). Those experiments had such a result that a system disturbed from equilibrium by a mechanical (ordered) work $W_i^{\mathrm{e}} = W_i^{\mathrm{e}}(\mathbf{R}_i)$ done on it returned to the initial equilibrium state after a heat amount Q strictly equivalent to the work had been removed from the system. Taking the work of both ordered and unordered character (according to the above classification) into consideration means the necessity to extend the space of variables wherein the above considered cyclic processes take place. It is easy to reveal in this case that integrand (2.1.2) constitutes a state function in the space of variables (Θ_i, $\mathbf{R}_i$), i.e. a more general one than the system internal energy. This function depends on both the internal Θ_i and external $\mathbf{R}_i$ system coordinates, i.e. constitutes the sum of the external and internal system energies. Such energy is usually called the *total* energy of the system. The decrease of the function $U=U(\Theta_i, \mathbf{R}_i)$ defines the sum of all (ordered and unordered) works the system do:

$$-\,dU(\Theta_i, \mathbf{R}_i) = \Sigma_i\, \text{đ}W_i^{\text{н}} + \Sigma_i\, \text{đ}W_i^{e}\,. \qquad (2.1.4)$$

According to this expression the energy of a system, in the absence of external impacts on the system ($\Sigma_i \text{đ}W_i^{\text{н}} = 0$, $\Sigma_i \text{đ}W_i^{\text{e}} = 0$), remains invariable at any variations of its state. In other words, the *energy of an isolated system is constant*. Thus the generalization of the heat and work equivalence principle to non-equilibrium systems directly leads to the law of conservation of “total” energy as a state function for the entire set of interacting (mutually moving) bodies. However, for such a system (isolated) all its energy is *internal*. This fact reveals the imperfection of dividing the energy into *external* and *internal*. From the position of thermokinetics considering the entire set of interacting bodies as a single non-equilibrium whole it is more important that its energy be measured in an *own* (absolute) reference frame not connected with the state of any of the bodies within the environment1). Since the term *system energy* with regard to the function $U(\Theta_i, \mathbf{R}_i)$ unambiguously tells the energy belongs to the system itself, the terms “total”, “external”, “internal”, etc energies become superfluous. This allows focusing on other properties of energy and its other components which characterize its conversion capacity.

2.2. Cancellation of Dissipative Terms in energy Balance Equations

Let us consider the consequences ensuing from the fact itself of existing the system energy $U(\Theta_i, \mathbf{R}_i)$ as a function of the quite certain set of arguments (state coordinates) As shown above, the energy of a heterogeneous system as a function of its state is generally expressed as $U = U\,[\mathbf{Z}_i(\Theta_i, \mathbf{S}_i, \boldsymbol{\varphi}_i)]$, where $i = 1, 2, \ldots, n$ – number of energy components equal

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1) Otherwise, should the Energy conservation be violated, the Energy of a system would vary with the state variation of these bodies despite the absence of Energy exchange with the system.

to the maximal number of independent processes for some of their categories (uniform processes, redistribution and reorientation processes). This means that the exact differential of energy may be expressed by the following relationship:

$$dU = \Sigma_i(\partial U/\partial \Theta_i)d\Theta_i + \Sigma_i (\partial U/\partial \mathbf{S}_i)d\mathbf{S}_i + \Sigma_i (\partial U/\partial \boldsymbol{\varphi}_i)d\boldsymbol{\varphi}_i. \qquad (2.2.1)$$

Derivatives of some system parameters (U) with respect to other ones (Θ_i, $\mathbf{S}_i$, $\boldsymbol{\varphi}_i$) are also system parameters. Therefore denoting them as:

$$\Psi_i \equiv (\partial U/\partial \Theta_i); \qquad (2.2.2)$$

$$\mathbf{F}_i \equiv -(\partial U/\partial \mathbf{S}_i); \qquad (2.2.3)$$

$$\mathbf{M}_i \equiv -(\partial U/\partial \boldsymbol{\varphi}_i), \qquad (2.2.4)$$

gives the fundamental identity of thermokinetics in the form:

$$dU \equiv \Sigma_i \Psi_i \, d\Theta_i - \Sigma_i \, \mathbf{F}_i \cdot d\mathbf{S}_i - \Sigma_i \, \mathbf{M}_i \cdot d\boldsymbol{\varphi}_i. \qquad (2.2.5)$$

For isolated systems the right-hand member of identity (2.2.5) becomes zero. For systems not changing its spatial orientation the two last terms in (2.2.1) and (2.2.6) may be combined ($\Theta_i d\mathbf{S}_i + \mathbf{Z}_i d\mathbf{e}_i = \Theta_i d\mathbf{R}_i$), then the fundamental identity of thermokinetics becomes:

$$dU \equiv \Sigma_i \Psi_i \, d\Theta_i - \Sigma_i \, \mathbf{F}_i \cdot d\mathbf{R}_i. \qquad (2.2.6)$$

Identities (2.2.5) and (2.2.6) are nothing else but a result of the joint definition of the related parameters Ψ_i and Θ_i, $\mathbf{F}_i$ and $\mathbf{S}_i$ or $\mathbf{Z}_i$, $\mathbf{M}_i$ and $\boldsymbol{\varphi}_i$. To clarify the physical meaning of the parameters thus introduced, let us first consider the particular case of internally equilibrium (spatially homogeneous) and stationary thermo-mechanical systems. Such simplest systems may be instantiated as the working media of heat engines in the vaporous or gaseous state. They have two degrees of freedom – thermal and mechanical, i.e. the capacity for the heat exchange Q and the uniform expansion work W_{ex}. Due to the absence of redistribution and reorientation processes in homogeneous systems ($d\mathbf{S}_i$, $d\boldsymbol{\varphi}_i = 0$) the parameters Ψ_i are the same for all points of such a system and equal to their local values ψ_i, so that identity (2.2.5) goes over into a joint equation of the first and second laws of thermodynamics for closed systems:

$$dU = \Sigma_i \, \psi_i \, d\Theta_i = TdS - pdV \, . \qquad (2.2.7)$$

Since the variation of the coordinates Θ_i in an equilibrium system is caused by exclusively the external heat exchange (their internal sources are absent), the terms of this relationship characterize, respectively, the elementary heat exchange in the system $đQ = TdS$ and the elementary expansion work $đW_{\mathrm{ex}} = pdV$. In this case the parameters Ψ_i acquire the meaning of the absolute temperature T and absolute pressure p. In the more general case of spatially heterogeneous systems the parameters Ψ_i are, as will be shown hereinafter, the generalized local potentials ψ_i averaged by mass in all elements of the system.

To clarify the meaning of the terms of the second sum in (2.2.5), we must take into account that they correspond to the redistribution processes running at constant parameters Θ_i and $\boldsymbol{\varphi}_i$, i.e. with invariable direction of the unit vector $\mathbf{e}$. Then $(\partial U/\partial \mathbf{S}_i) = \mathbf{e}\cdot(\partial U/\partial \mathbf{R}_i) = \mathbf{F}_i\cdot\mathbf{e}$, i.e. represents a projection of the resultant $\mathbf{F}_i$ on the direction of movement of the object Θ_i the force is applied to. Thus the terms of the second sum in (2.2.5) characterize the elementary useful work $đW_i^{\mathrm{e}} = \mathbf{F}_i\cdot d\mathbf{R}_i$ that has the same form as in mechanics. This work may be expressed in terms of the so-called thermodynamic forces $\mathbf{X}_i$ defined as:

$$\boldsymbol{X}_i \equiv -(\partial U/\partial \mathbf{Z}_i). \tag{2.2.8}$$

Since at Θ_i, $\boldsymbol{\varphi}_i$ = const, $(\partial U/\partial \mathbf{Z}_i) = \Theta_i^{-1}(\partial U/\partial \mathbf{R}_i) = \mathbf{F}_i/\Theta_i$, then the $\mathbf{X}_i$ thermodynamic forces thus introduced are actually the specific forces in their usual (Newtonian) meaning, i.e. the forces $\mathbf{F}_i$ per unit of the value Θ_i they transfer. These are, in particular, the specific mass, bulk and surface forces, for which the Θ_i value is construed as, respectively, mass M, volume V and surface f of the body. This category also includes the Lorenz force $\mathbf{F}_{\mathrm{e}}$ related to the electric charge Θ_{e} transferred. In the theory of irreversible processes such forces are termed the *thermodynamic forces in their energy representation* (Gyarmati, 1974). Using them enables representation of work by two equivalent expressions:

$$đW_i^{\mathrm{e}} = \mathbf{F}_i\cdot d\mathbf{R}_i = \mathbf{X}_i\cdot d\mathbf{Z}_i. \tag{2.2.9}$$

The work described by expression (2.2.9) may be mechanical, thermal, electrical, chemical, etc (depending on nature of the forces to overcome); external or internal (depending on where the forces arise – either in the system itself or outside); useful or dissipative (depending on what the work involves – either purposeful conversion of energy or its dissipation).

Lastly, the terms of the third sum in (2.2.5) correspond to the reorientation processes running with constant Θ_i and R_i. In this case $\mathbf{F}_i\cdot d\mathbf{R}_i = \mathbf{F}_i\cdot[d\boldsymbol{\varphi}_i,\mathbf{R}_i]$, and the parameter $\mathbf{M}_i$ acquires the meaning of a torque from the force $\mathbf{F}_i$:

$$\mathbf{M}_i = \mathbf{F}_i\times\mathbf{R}_i \tag{2.2.10}$$

This “torsion” torque is advisable to be called the “orientation” torque in the case it becomes zero when the direction of the force $\mathbf{F}_i$ coincides with the direction of the displacement vector $\mathbf{R}_i$.

The fundamental identity of thermokinetics thus obtained is valid regardless of what causes the variation of the parameters Θ_i, $\mathbf{S}_i$ and $\boldsymbol{\varphi}_i$ – either the external heat exchange or the internal (including relaxation) processes. Therefore it is applicable to *any processes* (both reversible and irreversible). At the same time it is most detailed of all the relationships connecting the parameters of spatially heterogeneous systems since it allows for *any possible categories of processes* running in such systems.

2.3. Distinction between Convertible and Inconvertible Parts of energy (inergy and anergy)

Due to the fact that thermokinetics rejects in its grounds the process idealization expressed in such notions as “quasi-static” (infinitely slow), “equilibrium” and “reversible” a possibility appears to introduce time as a logically consistent physical parameter into the equations of thermokinetics. For that it is enough to rewrite identity (2.2.5) in the form containing total derivatives of the state parameters earlier introduced with respect to time t:

$$dU/dt \equiv \Sigma_i \Psi_i \, d\Theta_i/dt - \Sigma_i \mathbf{F}_i \cdot \mathbf{v}_i - \Sigma_i \mathbf{M}_i \cdot \boldsymbol{\omega}_i \,. \qquad (2.3.1)$$

Here $\mathbf{v}_i \equiv \mathbf{e}_i d\mathrm{R}_i/dt$ – translation velocity of the energy carrier Θ_i; $\boldsymbol{\omega}_i \equiv d\boldsymbol{\varphi}_i/dt$ – angular velocity of its reorientation (or rotation). In the particular case, when the parameter Θ_i means mass of a system, the values $\mathbf{v}$ and $\boldsymbol{\omega}$ characterize its linear and angular velocity as a whole. For the future it is quite important to obtain the local statement of this identity true for any element of the continuum. For this purpose let us apply equation (2.2.5) first to the system where redistribution processes are absent. Then the second and the third sums in (2.2.5) disappear, and the identity becomes:

$$dU/dt. \equiv \Sigma_i \Psi_i \, d\Theta_i/dt. \qquad (2.3.2)$$

In the systems this equation represents the variation of the Θ_i[1)] parameters is caused by exclusively the transfer of some amount of energy carrier across the system borders. This allows representing the behavior of these parameters in the time domain by a known expression:

[1)] From the physical standpoint the value Θ_i that is actually the extensive measure of particular kind interaction (Energy) carrier is advisable to be called for short the *Energy carrier*. This will facilitate the understanding of many processes under investigation.

$$d\Theta_i/dt = -\int\mathbf{j}_i^{\mathrm{e}}\cdot d\mathbf{f}\,, \tag{2.3.3}$$

where $\mathbf{j}_i^{\mathrm{e}} = \rho_i\mathbf{v}_i$ – local density of flow of the energy carrier Θ_i through a vector element $d\mathbf{f}$ of the closed surface f in the direction of external normal **n; v**$_i$ – velocity of energy carrier transfer through the system surface element $d\mathbf{f}$ in stationary reference frame (Fig. 2.1).

Substituting (2.3.3) into (2.3.2) gives:

$$dU/dt = -\Sigma_i\Psi_i\int\mathbf{j}_i^{\mathrm{e}}\cdot d\mathbf{f}. \tag{2.3.4}$$

This equation is evidently a particular case of the more general expression

$$dU/dt = -\Sigma_i\int\psi_i\mathbf{j}_i^{\mathrm{e}}\cdot d\mathbf{f}, \tag{2.3.5}$$

when the local value ψ_i of generalized potential Ψ_i is the same for all system points and may therefore be factored outside the integral sign. The product $\psi_i\mathbf{j}_i$ is the i^{th} component of the energy flow density $\mathbf{j}_{\mathrm{e}} = \Sigma_i\,\psi_i\mathbf{j}_i$ through an element $d\mathbf{f}$ of the system surface f. Therefore changing in (2.3.4) to the integral taken over system volume as based on the Gauss-Ostrogradsky's theorem we come to the expression for the law of energy conservation for an arbitrary continuum area, which was proposed by N. Umov in 1873:

$$dU/dt = -\int\nabla\cdot\mathbf{j}_{\mathrm{e}}dV. \tag{2.3.6}$$

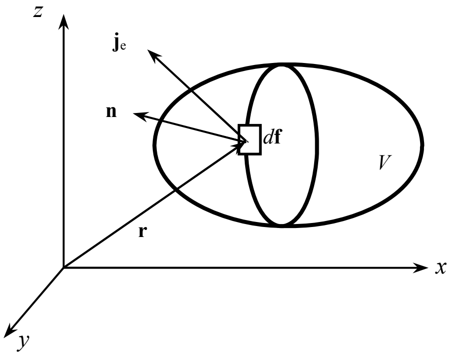

Fig. 2.1. Energy Flow across System Borders

According to this expression the system energy variation equals the amount of energy having passed across the system borders for that particular time. Or according to Umov himself, "energy flow…is caused by energy admission or release a medium provides across its borders". It should be noted that the validity of this statement is by no means restricted to the mechanical energy N. Umov meant.

This equation may be developed by representing the energy flow divergence $\nabla\cdot\mathbf{j}_{\mathrm{e}} = \Sigma_i\nabla\cdot(\psi_i\mathbf{j}_i^{\mathrm{e}})$ as a sum of two summands $\Sigma_i\,\psi_i\,\nabla\cdot\mathbf{j}_i^{\mathrm{e}} + \Sigma_i\mathbf{j}_i^{\mathrm{e}}\cdot\nabla\psi_i$:

$$dU/dt = -\Sigma_i\int\psi_i\,\nabla\cdot\mathbf{j}_i^{e}\,dV + \Sigma_i\int\mathbf{x}_i\cdot\mathbf{j}_i^{e}\,dV, \tag{2.3.7}$$

where

$$\mathbf{x}_i \equiv -\nabla\psi_i \tag{2.3.8}$$

is a local motive force of the i^{th} process expressed as negative gradient of generalized potential and named in the theory of irreversible processes as the "thermodynamic force in its energetic representation" (I. Gyarmati, 1974).

Equation (2.3.7) enables clarifying the meaning of the "global" variables Ψ_i and $\mathbf{X}_i$ introduced earlier for a system in whole. Taking into account that volume or mass elements in continuums do not change their spatial orientation ($d\boldsymbol{\varphi}_i = 0$) identity (2.2.6) may be expressed in the form:

$$dU/dt \equiv \Sigma_i\Psi_i\, d\Theta_i/dt - \Sigma_i\, \mathbf{X}_i\cdot\mathbf{J}_i\,, \tag{2.3.9}$$

where

$$\mathbf{J}_i \equiv \Theta_i\mathbf{e}_i dR_i/dt = \Theta_i\mathbf{v}_i\,, \tag{2.3.10}$$

i.e. are total flows of displacement (transfer) of the i^{th} energy carrier Θ_i.

These flows at $d\boldsymbol{\varphi}_i = 0$ may be expressed in terms of their densities $\mathbf{j}_i \equiv \rho_i d\mathbf{r}_i/dt$ through the evident relationship:

$$\mathbf{J}_i \equiv \Theta_i d\mathbf{R}_i/dt = \int(d\mathbf{r}_i/dt)d\Theta_i = \int \mathbf{j}_i\, dV\,. \tag{2.3.11}$$

It is easy to see that the flows $\mathbf{J}_i$ differ in their dimensions from the more usual notion of flow rate and in their meaning as per (2.3.10) are closer to the "generalized momentum" $\mathbf{P}_i = \Theta_i\mathbf{v}_i$ of the i^{th} energy carrier Θ_i for a system in whole. Such flows play an important role in many phenomena. These are, e.g., the vector flows of electric displacement in a system with the volume V defined by the product of the system free charge Θ_e and the velocity of its center displacement in the free charge redistribution processes. This is the value, to which the following parameters are proportional: magnetic field induction vector (Biot-Savart law), Thomson–Joule heats in conductors and thermo-elements, electromagnetic force driving a conductor with current (Ampere's law), etc. We will hereinafter be referring to them time and again when dealing with the transfer and conversion of energy in any forms, which will confirm the necessity and usefulness of generalizing the Maxwell's displacement current concept to phenomena of other nature.

To find the relation between the "global" (pertaining to a system in whole) and the local thermodynamic forces $\mathbf{x}_i$, let us take into account that the parameters Ψ_i in identity (2.3.5) are defined for the coordinates $\mathbf{Z}_i$ being constant, i.e. for the difference $\rho_i(\mathbf{r},t) - \rho_{i0}(t)$ invariable in all points of the system volume V. From this it follows that in the expression

$$d\Theta_i/dt = \int (d\theta_i/dt)\, \rho dV\,, \qquad (2.3.12)$$

the specific parameters θ_i vary uniformly in all parts of the system, so that $d\theta_i/dt$ may be factored outside the integral sign. Hence,

$$\Psi_i = \mathrm{M}^{-1} \int \psi_i dM\,, \qquad (2.3.13)$$

being the system mass-averaged value of the local potential ψ_i. Similarly proceeding from the invariance of the process power $N_i = \mathbf{X}_i \cdot \mathbf{J}_i$ when representing it in terms of the local and global parameters

$$\mathbf{X}_i = \mathbf{J}_i^{-1} \int \mathbf{x}_i \cdot \mathbf{j}_i \, dV, \qquad (2.3.14)$$

gives that the "global" thermodynamic force $\mathbf{X}_i$ is some averaged value of the local thermodynamic force $\mathbf{x}_i \equiv -\nabla\psi_i$.

The relationship thus obtained between the local variables the field theories operate with and the thermodynamic parameters characterizing the state of a continuum in whole opens the possibility of describing their properties from the positions of thermokinetics. In this case particular importance is attached to introducing in thermodynamic equations the most significant for natural science in whole concepts of flows $\mathbf{J}_i$,$\mathbf{j}_i$ as generalized rates of the transfer processes and the concept of power (capacity) of the energy conversion process in a whole system $N_i = \mathbf{X}_i \cdot \mathbf{J}_i$ and in its unit volume $\mathbf{x}_i \cdot \mathbf{j}_i$. It should be noted that the notion of capacity refers to only the useful energy conversion processes and, therefore, could not appear in the depths of the theory of irreversible processes restricted to consideration of exclusively dissipative phenomena. On the contrary, all basic relationships of this theory will hereinafter be obtained as a consequence from thermokinetics (Chapter 4).

2.4. Elimination of Dissipative Terms from energy Balance Equations

In non-equilibrium systems the majority of the state parameters Θ_i and $\mathbf{R}_j$ vary due to not only energy interchange between the systems and the environment, but also in relaxation processes running in them, i.e. spontaneously. In particular, the system volume may increase with no work done, but due to expansion into void, the mass M_k of the k^{th} substances – due to chemical reactions running in the system, the entropy S – due to conversion of ordered forms of energy into chaotic (thermal) form, the displacement vectors $\mathbf{R}_i$ – due to equalization of distributing the above parameters over the system. This fact is usually taken into account by the so-called balance equations, which integral form looks like:

$$d\Theta_i = d_e\Theta_i + d_u\Theta_i\,, \tag{2.4.1}$$

$$d\mathbf{R}_i = d_e\mathbf{R}_i + d_u\mathbf{R}_i\,. \tag{2.4.2}$$

Here $d_e\Theta_i$ – two-sided variations of the Θ_i coordinates caused by external energy exchange (heat transfer, expansion work, mass transfer, etc.); $d_e\mathbf{R}_j$ – similar variations of the $\mathbf{R}_j$ coordinates caused by useful work of the i^{th} kind; $d_u\Theta_i$, $d_u\mathbf{R}_j$ – one-sided spontaneous variations of the same parameters caused by running internal (relaxation) processes and, depending on sign, named usually either "wells" or "sinks" of corresponding parameters.

Expression (2.4.2) may be more conveniently represented as the flow balance equation:

$$\mathbf{J}_i = -\,\mathbf{J}_i^{\mathrm{e}} + \mathbf{J}_i^{\mathrm{p}}\,, \tag{2.4.3}$$

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

To derive the differential form of balance equation (2.4.1), let us represent the equation in the form:

$$d\Theta_i/dt = -\int \nabla\cdot\mathbf{j}_i^{\mathrm{e}}\,dV + \int \sigma_i\,dV, \tag{2.4.4}$$

where the augend corresponds to the term $d_e\Theta_i/dt$ and the addend – to $d_u\Theta_i/dt$; σ_i – density of internal wells or sinks Θ_i.

To change over from the integral form of (2.4.4) to the differential one, let us represent the Θ_i as the integral $\int\rho_i dV$, where $\rho_i = (\partial\Theta_i/\partial V) = \rho_i(V,t)$ – density of the Θ_i value. We are going to consider a continuum, which mass elements $dM = \rho dV$ remain invariable during its deformation (such a description is named spatial or Lagrangian). Then $d\Theta_i/dt = \int(d\theta_i/dt)\rho dV$, and one can write instead of (2.4.3):

$$\rho d\theta_i/dt + \nabla\cdot\mathbf{j}_i^{\mathrm{e}} = \sigma_i\,. \tag{2.4.5}$$

where $\mathbf{j}_i^{\mathrm{e}} = \rho_i\mathbf{w}_i$ – density of the energy carrier flow across the borders of the system elements; $\mathbf{w}_i = \mathbf{v}_i - \mathbf{v}$ – velocity of the value Θ_{i} transfer relative to the moving border of a system element. Equation (2.4.5) is called the substantial equation describing balance of some field value Θ_i.

In the similar way one can change over to the differential form of balance equation (2.4.3) allowing for relationship (2.3.11):

$$\mathbf{j}_i = -\mathbf{j}_i^{\mathrm{e}} + \mathbf{j}_i^{\mathrm{p}} \,. \qquad (2.4.6)$$

Substituting balance equations (2.4.5) and (2.4.6) into (2.3.7) and considering that, as in (2.3.12), $d\theta_i/dt$ is constant all over the bulk of the system and factoring the mean-mass potential Ψ_i and the force $\mathbf{X}_i$ out of the integral sign gives according to (2.3.14):

$$dU/dt = \Sigma_i\!\int\psi_i\,(d\theta_i/dt)\rho dV - \Sigma_i\!\int\mathbf{x}_i{\cdot}\mathbf{j}_i dV - \Sigma_i\!\int\psi_i\sigma_i dV + \Sigma_i\!\int\mathbf{x}_i{\cdot}\mathbf{j}_i^{\mathrm{p}} dV =$$

$$= \Sigma_i\Psi_i\, d_{\mathrm{e}}\Theta_i/dt - \Sigma_i\mathbf{X}_i{\cdot}\mathbf{J}_i - \Sigma_i\!\int\psi_i\sigma_i dV + \Sigma_i\!\int\mathbf{x}_i{\cdot}\mathbf{j}_i^{\mathrm{p}} dV. \qquad (2.4.7)$$

Comparing this expression with (2.3.9) gives that the last two of its terms containing wells and sinks of various coordinates mutually balance. From here the relation ensues between the wells and the sinks of various state coordinates:

$$\Sigma_i\, \psi_i\sigma_i = \Sigma_i\, \mathbf{x}_i{\cdot}\mathbf{j}_i^{\mathrm{p}} \,, \qquad (2.4.8)$$

which will hereinafter (Chapter 5) directly lead to the dissipative function expression as fundamental for the theory of irreversible processes.

Due to the mutual balance between the wells and the sinks of various coordinates thermokinetic identity (2.2.9) remains valid even when the variation of its terms is caused by internal (irreversible) processes. In other words, the thermodynamic identity *remains valid within the entire spectrum of real processes* – from "quasi-reversible" to critically irreversible.

2.5. Ordered and Unordered energy (inergy and anergy) as Characteristic Functions

The fact energy lost its primary meaning as a measure of capacity for work after the notions of internal and dissipation energy have been introduced engendered the problem to find a measure of motion or interaction, which would characterize such an important property of energy as its capacity for ordered (useful) work. The notion of external energy should have seemingly got the goals. The external energy was construed as that part of the energy of a system which did not depend on its internal state and was defined by exclusively the motion or position of the system as a whole relative to other bodies. As in mechanics, the external energy was defined by the useful external work a system could do when transiting from one configuration into another (adopted for a reference frame). The internal energy was accordingly construed as another part of the energy which did not depend on the position or motion of a system relative to other bodies and was defined by exclusively the internal (latent) motion and interaction of particle comprising the system. Since in equation (1.3.4) the internal energy played the role of dissipation energy, i.e. the energy that lost its capacity for work, it was equivalent to its division into workable and unworkable parts. However, later it became clear that a part of external energy, nevertheless, depends on the internal state of the system. E.g., in dielectric and magnetic materials the resulting electrical and magnetic field depends on the temperature of these bodies. In this case the polarization and magnetization work of these bodies involves a work done against external fields, i.e. changes both the external and internal energies. In some particular cases the situation could be simplified by introducing an additional notion of "internal self-energy of such bodies without field energy in vacuum" (I. Bazarov, 1991 et al). However, this energy, strictly speaking, is not anymore a "self-energy" since the external field has already been changed by the polarized or magnetized bodies available therein. Furthermore, with the advent of the specific theory of relativity it was revealed moving bodies did not feature at all a whatever part of energy which would not depend on the rate of their motion. (R. Tolman, 1974).

As a result, the energy irreversibility and dissipation phenomena – most fundamental for thermodynamics and natural science – have become non-interpretable in whole as resulting from the conversion of *external* energy into *internal*. The way out of the situation was seen for a long time as the idea offered by H. Helmholtz and consisted in the division of energy into a "free" part" $\Gamma = U - TS$ and a "bound" (to heat motion) part TS. As will be shown in Chapter 4, the decrease of the Helmholtz free energy F under certain conditions actually defines the capacity of systems for reversible work. However, with the arbitrariness classic thermodynamics tolerates in choosing the internal energy reference frame the bound energy value TS appears in many cases to be in excess of the internal energy itself (K. Putilov, 1974). Under these conditions this may not be considered as a part of internal energy. The same may be also said of the Gibbs' "free enthalpy" $G = H–TS$ (where $H = U + pV$ is enthalpy). Furthermore, in open systems these state functions do not define anymore the work a particular system does (G. Gladyshev, 1988; I. Bazarov, 1991). In this connection the division of energy into "free" and "bound" loses its heuristic value in many respects.

The situation was not saved with the notion of *exergy* subsequently introduced (Z. Rant, 1955) as the maximal work a system can do before complete thermodynamic equilibrium with the environment has been obtained. The remainder unworkable part of the system energy Rant termed as *anergy*. The exergy and the anergy of a system define its *technically usable* and *unusable* parts, respectively. However, their values depend on not only the parameters of a system itself, but on the parameters of the environment as well so that the exergy is not the function of state of a system itself. Furthermore, the exergy does not at all define the capacity of a system itself to do work since depends on the amount of heat supplied to the system from outside in the process of its work. And what is more, the exergy may even be a negative value (unlike the energy) if the intensive parameters of the system (e.g., its temperature) are below the same of the environment. We say nothing of the difficulties in calculating the exergy under inconstant environmental conditions, as well as of the arbitrariness in choosing its reference point under the conditions when environmental parameters substantially differ for different points of the planet. As a result, the division of energy into exergy and anergy has not either gained a wide spread.

A solution to the said problem becomes possible when changing over to studying non-equilibrium systems and introducing additional non-equilibrium state parameters of spatially heterogeneous media $\mathbf{X}_i$ and $\mathbf{Z}_i$. Let us assume that we deal with a spatially homogeneous medium ($\mathbf{X}_i = 0$) where the generalized potential values Ψ_i are the same for all points, i.e. equal to their equilibrium values $\bar{\Psi}_i$. For such a system in the form of (2.2.9) instead of identity (2.2.6) the following equation is available:

$$d\bar{U} = \Sigma_i \bar{\Psi}_i \, d\Theta_i, \tag{2.5.1}$$

where $\bar{U}$ – equilibrium part of the energy in non-equilibrium system.

The right-hand terms of this equation characterize the equilibrium heat exchange between the system and the environment. The term “equilibrium” means that at $\mathbf{X}_i \to 0$ processes are running infinitely slowly (quasi-statically) and, therefore, do not disturb the spatial homogeneity of the system ($\mathbf{Z}_i \to 0$). The work of these processes refers to the *unordered* category due to the absence of a resultant of the forces to be overcome in homogeneous systems. The work of such a kind involves introducing the k^{th} substance across the system borders (when not only the cubic strain occurs, but the interparticle interaction forces are also overcome), electrical charge introduced, uniform compression, mass transfer, momentum convective transfer along with the mass introduced, and heat exchange we attribute to the “micro-work” category on the grounds that heating of a body accelerates the chaotic motion of particles.

Applying the Legendre transformation to the above summands $\bar{\Psi}_i d\Theta_i = d\bar{\Psi}_i \Theta_i - \Theta_i d\bar{\Psi}_i$ in the extreme case of $\mathbf{X}_i = 0$ and $\Psi_i = \bar{\Psi}_i$ gives:

$$d(\bar{U} - \Sigma_i \bar{\Psi}_i \Theta_i) = - \Sigma_i \Theta_i d\bar{\Psi}_i . \tag{2.5.2}$$

This expression refers to a system with no work done on, which could disturb it from equilibrium. Hence, according to the self-non-disturbance axiom both parts of (2.5.2) become zero. From this it follows that the equilibrium part of system energy $\bar{U}$ up to a constant (which could be assumed equal to zero) is defined as:

$$\bar{U} = \Sigma_i \bar{\Psi}_i \Theta_i = \Sigma_i \bar{U}_i. \qquad (2.5.3)$$

According to (2.5.3) the unordered energy of a system is the sum of the system component energies $\bar{U}_i = \bar{\Psi}_i \Theta_i$ (by the number of degrees of freedom), each being defined as the product of the momentum (interaction) of a particular kind Θ_i by the potential $\bar{\Psi}_i$ as a measure of its intensity. The value $\bar{U}_i$ characterizes the part of the non-equilibrium system energy left after the completion of all relaxation processes in the system (equalization of all potentials and completion of all chemical and the like internal transformations) and unable to do useful (ordered) work. Therefore we will call it the *unordered* energy or (for short) the *anergy*.

The remainder part of the system energy $E = (U - \bar{U})$ is *ordered*, i.e. capable of doing ordered work. This part of the system self-energy will be called (for short) the *inergy*[1)]. The fact of its order shows in the energy dissipation phenomenon meaning transformation of motion into unordered form. To express the ordered and unordered energies in terms of state parameters, let us consider that the spatial heterogeneity parameters $\mathbf{F}_i$ or $\mathbf{R}_i$ appear in the expression for the system energy U as a consequence of the uniform distribution of the usual "thermostatic" parameters Θ_i all over the system volume V (Chapter 1). When a system "contracts" to a material point ($V \rightarrow 0$), the parameters $\rho_i(\mathbf{r},t) \rightarrow \rho_{i0}(t)$ and $\mathbf{R}_i \rightarrow 0$. This means that in themselves the bulk elements of a heterogeneous system feature the same set of the variables Θ_i as in the homogeneous state. Hence, the unit volume energy as a function of the local variables ψ_i and $\Theta_i = (\partial\Theta_i/\partial M)$ has the same form of (2.5.4) as for an equilibrium system, while the energy of the system as a whole is expressed through the integral:

$$U = \Sigma_i \int \psi_i \, \theta_i \, \rho dV. \qquad (2.5.4)$$

This part of the system energy may be represented in the even shorter form:

$$U = \Sigma_i \tilde{\Psi}_i \Theta_i, \qquad (2.5.5)$$

[1)] In contrast to the Anergy, this term reflects the capacity of a system for *internal* work, i.e. for transmutations of Energy (including the dissipation character). It is evident that a system not having this ability can not either participate in the Energy exchange involved in these processes, i.e. can not do *useful internal work*.

if factoring outside the integral sign in (2.5.5) some "mean-energy" value of the generalized potential $\tilde{\Psi}_i = U_i/\Theta_i$ (not coinciding, in the general case, with Ψ_i. Then the system ordered energy as a state function becomes:

$$E = \Sigma_i (\tilde{\Psi}_i - \Psi_i)\Theta_i . \tag{2.5.6}$$

The ordered energy of non-equilibrium systems should also be complemented with chemical, atomic, nuclear, etc types of system energy. These types as well have the capacity for work and dissipation just as the energy of motion and interaction between macroscopic parts of the system. Chemically reacting media, spontaneously fissionable nuclear fuels, optically excited and ionized gases, etc are *non-equilibrium* even if spatially homogeneous. The non-equilibrium of such a kind existing in each of the system bulk elements and not associated with the spatial heterogeneity of the system as a whole will hereinafter be called *local*. To describe the state of locally non-equilibrium systems, it is also necessary to introduce special parameters of non-equilibrium. Here comes, in particular, the *completeness degree (intensity, range*, etc) of the r^{th} chemical reaction ξ_r. The similar coordinates may be introduced for phase transitions (V. Etkin, 1991). As will be clearly shown hereinafter, the scalar nature of such state coordinates will impose certain constraints on the possible conversion of such forms of energy into ordered work.

As seen, the thermokinetic approach makes superfluous such notions as external and internal, free and bound energies, Gibbs' energy and exergy superseding them by the intuitively comprehensible terms of ordered and unordered energies. Another nontrivial consequence of such an approach consists in the conclusion there is an ordered and unordered component in any of the i^{th} forms of matter motion including the internal thermal energy U_{T} that in thermal physics has always been entirely attributed to the chaotic form of motion and, therefore, considered as an entirely depreciated (degraded) energy. Meanwhile, thermal energy has also an ordered part that depends on the temperature gradients or drops in a system. In itself the fact a thermally heterogeneous system is able to do useful work has been known yet since S. Carnot (1824) who expressed it as, "all over where a temperature difference is available, the "living force" (i.e. the thermal "motive force" *(author's note)*) may also appear". In thermal relaxation processes this ordered part of thermal energy dissipates (degrades) just as other ordered forms of energy. This phenomenon may be experimentally confirmed by, e.g., the so-called *measurable heat content rise effect* (L. Brovkin, 1960, 1964).

In series of his experiments Brovkin discovered a phenomenon unexplainable from the classic thermodynamic standpoint and consisting in increasing mean-integral temperature in the process of thermal relaxation of an isolated thermally heterogeneous system. The experiments were conducted as follows. A resistance temperature detector sensing element was inserted into the gap of a closely packed roll of paper, cardboard, rubber tape or other sheet materials all over their length. Then the roll was subjected to irregular heating from an external heat source followed by the spontaneous process of thermal relaxation. In that process the resistance variation for such a "distributed" thermometer was registered. Surprising was the fact that for all of the materials tested a considerable (up to 17%) rise of the mean-integral temperature was observed. That rise had continued for tens of minutes until the temperature fall due to cooling of the specimen not quite thermally protected became dominating. The experimental results were attempted to have been explained by the dependence of thermal capacity of the materials on the temperature gradients therein and were construed as a rise of "measurable" (i.e. different from actual) heat content (enthalpy) of the system. Meanwhile, the experimental results directly demonstrated the rise of unordered part of internal thermal energy (analog of the Helmholtz's "bound" energy) due to the decrease in its ordered part (analog of his "free" energy).

The fact the ordered E and unordered $\bar{U}$ energies belong to the non-equilibrium state functions with the exact differential properties incident to them in this connection makes it possible to generalize the classic method of characteristic functions to spatially heterogeneous (in their properties) systems with an arbitrary number of degrees of freedom. The characteristic functions are construed in thermodynamics as such state functions of a system, mathematical operations on which allow direct definition of fundamental properties of this system. In itself the term *characteristic function* was introduced by Massier (1969), who first realized those functions as convenient to be used in finding the system parameters as their derivatives. One of such characteristic functions is the system energy U itself, which complete variation in any processes is represented by (2.2.5). In accordance with (2.2.5) and (2.2.3) the reason why any of the i^{th} non-equilibrium processes arises – the generalized force $\mathbf{F}_i$ – may be found as the derivative of system energy with respect to the displacement vector $\mathbf{R}_i$ under the constancy of other similar vectors $\mathbf{R}_j$ and all "thermostatic" coordinates Θ_i.

In the similar way the derivatives of the system anergy U with respect to the "thermostatic" coordinates Θ_i under the constancy of other similar coordinates Θ_i and all displacement vectors $\mathbf{R}_i$ allow finding the generalized potentials for the non-equilibrium state of the system:

$$\Psi_i = (\partial U/\partial \Theta_i). \qquad (2.5.7)$$

In the particular case when Θ_i constitutes the heat exchange coordinate Θ_T (entropy) expression (2.5.6) defines the absolute temperature T of the system:

$$T = (\partial U/\partial\Theta_T). \qquad (2.5.8)$$

In the other particular case when $\Theta_i = \Theta_p = V_o - V$ (where V_o means the theoretical compression limit) this derivative allows definition of the absolute pressure p in the system:

$$p = (\partial U/\partial\Theta_p). \qquad (2.5.9)$$

The second derivatives of the energy U with respect to the coordinates Θ_i allow finding other thermodynamic properties of thermodynamic systems. In particular, for a thermo-mechanical system, where $U = U(S,V)$, the second derivative of U with respect to entropy under the constancy of volume and other equilibrium coordinates allows finding the isochoric heat capacity C_V of the system:

$$(\partial^2 U/\partial S^2)_V = (\partial T/\partial S)_V = T/C_V. \qquad (2.5.10)$$

Due to the breakdown of energy into the ordered and unordered components we receive in addition to it two more characteristic functions $E = \Sigma_i E_i$ and $\bar{U} = \Sigma_i \bar{U}_i$, where E_i, $\bar{U}_i$ – components of E and $\bar{U}$, which we will hereinafter call the *partial* energies (of the i^{th} kind). These functions known allow to solve the same problems as the energy under less strict constraints. In particular, the forces $\mathbf{F}_i$ can be found as the derivatives of ordered energy

$$\mathbf{F}_i = -(\partial E/\partial \mathbf{R}_i) = -(\partial E_i/\partial \mathbf{R}_i), \qquad (2.5.11)$$

omitting in the first case the constancy requirement for all thermostatic variables Θ_i and in the second case – the constancy requirement for all other displacement vectors $\mathbf{R}_j \neq \mathbf{R}_i$. Furthermore, U replaced by E_i allows finding the internal forces $\mathbf{F}_i$ acting within isolated systems (where $dU = 0$). In mechanical systems, where the ordered energy E is identical to the potential energy of the system, the above expression goes over into the standard force expression in mechanics (L. Landau, E. Livshits, 1973).

Another valuable property of the characteristic functions E and $\bar{U}$ is that they may serve as thermodynamic potentials, i.e. as the values, which decrease defines the maximal work a system can do. In particular, the decrease of the ordered energy E defines the sum of all kinds of the useful external W_i^{e} and the dissipative external W_i^{D} works the system do:

$$-dE = \Sigma_i \mathbf{X}_i \cdot d\mathbf{Z}_i = \Sigma_i đW_i^{\text{e}} + \Sigma_i đW_i^{\text{D}}. \qquad (2.5.12)$$

From this it follows that the ordered energy of a system is measured by the value of the maximal useful external work W_i^{e} the system can do subject to the reversible (dissipativeless) character of this process ($W^{\mathrm{D}} = 0$). This makes the notion of ordered energy related to the *external energy* $E^{\mathrm{k}} + E^{\mathrm{p}}$ in mechanics. However, firstly, unlike mechanical systems, where the external energy does not depend on the internal state of the system, the ordered energy in the generally polarized, magnetized, irregularly deformed, etc media vary with the variation of temperature, composition and other internal parameters of the system. Secondly, from the positions of thermokinetics considering as a system the whole set of investigator's interest comprising interacting (mutually moving) bodies or body's parts the notion of external energy is devoid of sense. Indeed, the external energy by definition depends on the motion of the system or its position relative to the environment, i.e. is "mutual" and may be ascribed to one of them in only the simplest case. Therefore, when the environment is included in the "extended" non-equilibrium system the external energy becomes an ordered part of its "self-energy" U not depending on the environment. Accordingly we will refrain from using the term "external energy" where it might cause misunderstanding. Similarly the decrease of the unordered energy $\bar{U}$ defines the maximal external unordered work a system can do on the environment subject to the reversible character of the process.

The advantage of representing thermodynamic potentials in terms of ordered and unordered energy becomes apparent when allows finding the ordered W_i^{e} and unordered $W_i^{\text{н}}$ work for each of its i^{th} forms. In this respect they stand out from the Gibbs and Helmholtz free energies in classic thermodynamics, which decrease characterizes just their sum of W^{e} and $W^{\text{н}}$. It is significant that in this case the energy components introduced herein can be found for *any current state of the system* by known fields or distribution function for the energy carrier Θ_i and known equations of system state in the general form as $\psi_i = \psi_i(\theta_1, \theta_2, \ldots, \theta_n)$. In particular, the potentials Ψ_i can be found as mean-mass values of the local potential ψ_i, while the potentials Ψ_i – as their "mean-energy" values. To find them, the equations are used interconnecting the variables ψ_i and Θ_i similar to the equations of ideal and real gas state.

The further advantage of representing characteristic functions in terms of the non-equilibrium parameters becomes apparent when revealing a whole class of internal conversion processes involved in the external energy exchange. As expressions (2.5.1) and (2.5.2) show, the partial energy of any degree of freedom $\bar{U}_i$ can vary both as a result of the external action $d\bar{U}_i^{\mathrm{e}} = \bar{\Psi}_i \, d\Theta_i$ and due to the thus caused *internal conversions* of this energy into other forms ($d\bar{U}_i^{u} = \Theta_i \, d\bar{\Psi}_i$). In this case

$$-\Sigma_i\, \Theta_i\, d\bar{\Psi}_i = 0. \tag{2.5.13}$$

This expression generalizes a known Gibbs-Duhem's relationship (I. Bazarov, 1991) earlier obtained for the particular case of open thermomechanical systems to the polyvariant equilibrium systems with any finite number of degrees of freedom. However, the sense of this relationship from the energy standpoint as the law of energy conservation at internal energy conversions from one form into another becomes clear with only introducing the notion of partial energy. The existence of such internal conversions by no means follows from classic thermodynamics since classic thermodynamics proceeds from the assumption that quasi-static impacts such as $\bar{\Psi}_i\, d\Theta_i$ do not disturb equilibrium in a system and, therefore, can not engender whatever internal processes therein. Meanwhile, for the isolated systems thermokinetics considers studying internal energy conversion processes of such a kind is brought to the forefront because of no other processes existing in such systems. Therefore, it seems to be important to demonstrate that expression (2.5.13) represents nothing else but the energy conversion processes that acquire the quasi-static character in equilibrium systems

According to (2.5.4) the rate of system energy variation dU/dt is derived as:

$$\frac{dU}{dt} = \sum\nolimits_i \int_V \psi_i \frac{d\theta_i}{dt} \rho dV + \sum\nolimits_i \int_V \theta_i \frac{d\psi_i}{dt} \rho dV. \tag{2.5.14}$$

Since in non-equilibrium systems the potentials ψ_i are a function of the field point radius vector $\mathbf{r}$ and time t, then:

$$\frac{d\psi_i}{dt} = \left(\frac{\partial \psi_i}{\partial t}\right)_{\mathbf{r}} + \left(\frac{\partial \psi_i}{\partial \mathbf{r}}\right)_t \frac{d\mathbf{r}}{dt} \tag{2.5.15}$$

Substituting (2.5.15) into (2.5.14) and allowing for $(\partial\psi_i/\partial\mathbf{r}) = -\mathbf{x}_i$; $d\mathbf{r}/dt = \mathbf{v}_i$ gives:

$$\frac{dU}{dt} = \Sigma_i \int \psi_i \frac{d\theta_i}{dt} \rho dV - \Sigma_i \int \mathbf{x}_i \cdot \mathbf{j}_i dV + \Sigma_i \int \theta_i \frac{\partial \psi_i}{\partial t} \rho dV. \tag{2.5.16}$$

Comparing this expression with (2.4.7) gives that the last sum in (2.5.16) becomes zero owing to equality (2.4.8), i.e. due to the mutual balance of the terms containing wells and sinks of various coordinates:

$$\Sigma_i \int \theta_i(\partial\psi_i/\partial t)\,\rho dV = -\,\Sigma_i \int \psi_i\sigma_i\, dV + \Sigma_i \int \mathbf{x}_i{\cdot}\mathbf{j}_i^{\mathrm{p}} dV = 0. \qquad (2.5.17)$$

This expression is the further generalization of the Gibbs-Duhem's relationship to spatially heterogeneous systems when the potentials become a function of the point $\psi_i = \psi_i(\mathbf{r}, t)$. It reflects the fact that during the internal conversions of the ordered energy forms ($\mathbf{x}_i{\cdot}\mathbf{j}_i^{\mathrm{p}}$) into the unordered ones ($\psi_i\sigma_i$) the energy of the system remains invariable (in strict compliance with the law of its conservation)[1]. At the same time this relationship once again confirms that such conversions are possible in only spatially heterogeneous systems (where $\mathbf{x}_i \neq 0$). This means that the Gibbs-Duhem's classic relationship refers to the case of quasi-static processes when $\mathbf{j}_i^{\mathrm{p}} \to 0$. It is this internal conversion of energy that makes sense for the Gibbs-Duhem's generalized relationship from the energy standpoint.

2.6. Definition of General Form for Equations of State and Transfer

The above-developed body of mathematics is in itself insufficient for the investigation of particular processes. For that uniqueness conditions are required enabling to complete the set of the thermokinetic equations. Although thermokinetics imports these uniqueness conditions from outside it, nevertheless, dictates certain requirements for the number, general form and character of such uniqueness conditions.

The equations of state describing systems under investigation are the fundamental component of the uniqueness conditions. They reflect the relationship between the variables entering into thermodynamic identity (2.2.5) or (2.2.6). The total number of such equations is defined by the number of the independent variables entering into this identity, i.e. by the number of the independent processes really running in a system being described. Particular form of these equations is found by experimental or theoretically experimental way based on the simulation procedures including those of statistically mechanical character.

To go on with, let us restrict the consideration to an ample spectrum of systems lacking the reorientation processes. Let us assume the experimental investigation of such a system has revealed n transfer or redistribution processes running in it ($i = 1, 2, \ldots, n$). Then according to identity (2.2.5) or (2.2.9) the total number of variables characterizing the state of the system and its energy E is generally equal to $2n$. However, due to the constraints imposed some number of the processes of one of these categories may be

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[1] Hereinafter (Chapter 10) this will facilitate the understanding that thermal Energy is inevitably converted into its ordered forms when bodies accelerate up to the relativistic velocities.

absent. Let us assume the number of the transfer processes is n_i ($i = 1, 2,..., n_i$), while the same of the redistribution processes – n_j ($j = 1, 2,..., n_j$). Then the total number of the variables entering into identity (2.2.9) is equal $2(n_i+n_j)$. Since only (n_i+n_j) of them are independent, there must exist for such a system n_i equations interconnecting the variables Ψ_i and Θ_i and having the general form as:

$$\Psi_i = \Psi_i(\Theta_i, \mathbf{R}_j)\ , \tag{2.6.1}$$

and n_j equations interconnecting the variables $\mathbf{X}_i$ and $\mathbf{Z}_i$ and having the general form as:

$$\mathbf{X}_i = \mathbf{X}_i(\Theta_i, \mathbf{R}_j)\ . \tag{2.6.2}$$

Relations (2.6.1) may be instantiated by Clapeyron-Mendeleev's law and Van der Waals' law for gases, while relations (2.6.2) – by Hooke's law for elastic bodies, Curie-Weiss' law for dielectrics, etc. The fact itself such equations exist enables definition of a number of relations between physicochemical properties of the systems under investigation. These are, e.g., the relations between thermal coefficients of expansion for gases or isothermal compression coefficients and coefficients of elasticity in thermodynamics of solid bodies (Bazarov I.P., 1991).

When studying non-static processes, together with the equations of state it is necessary to know those relating velocity of some process with its motive forces. These equations include the laws of transfer of heat, charge, the k^{th} substance, momentum, etc. (Fourier's, Ohm's, Fick's, Newton's laws, etc.). They relate the generalized velocity of vector processes of heat conduction, electric conduction, diffusion and viscous friction. Arrenius' law relating the velocity of some r^{th} homogeneous chemical reaction w_r with its affinity A_r is an example of the scalar process equation. Fundamental equations of thermokinetics (2.2.5) and (2.2.6) without such empirical laws are equally as barren as the unified equation of the first and second laws of thermodynamics in the absence of the equations of state of the systems under investigation. The particular form of the transfer equations is derived *a posteriori* (from experience). However, thermokinetics makes certain demands on the number and general form of such equations imposing some constraints on the character of the interrelation between the state parameters these equations contain. In fact, having equations of state (2.6.1) and (2.6.2) at our disposal, let us represent the displacement vectors $\mathbf{R}_j$ as a function of n_i coordinates Θ_i and n_j motive forces $\mathbf{F}_j$:

$$\mathbf{R}_i = \mathbf{R}_i(\Theta_i, \mathbf{F}_j) \quad (i = 1,2,..., n_i; j = 1,2,..., n_j). \tag{2.6.3}$$

Taking total derivative of both parts of this expression with respect to time and keeping in mind that in stationary processes (where Ψ_i, $\mathbf{F}_j$ =const) these derivatives refer to the value $\mathbf{R}_i$ only and characterize velocity of the i^{th} transfer process $\mathbf{w}_i = d\mathbf{R}_i/dt$ gives:

$$\mathbf{w}_i = \mathbf{w}_i(\Theta_i, \mathbf{F}_j) \quad (i = 1,2,..., n_i; j = 1,2,..., n_j). \tag{2.6.4}$$

Respectively, the displacement flow $\mathbf{J}_i \equiv \Theta_i d\mathbf{R}_\mathrm{i}/dt$ may be defined as:

$$\mathbf{J}_i = \mathbf{J}_i(\Theta_i, \mathbf{F}_j) . \tag{2.6.5}$$

This relationship reflects the general form of the transfer laws ensuing from the equations of state of the system under investigation. The particular form of these equations is derived *a posteriori*. However, the fact itself of existing equations for the flows $\mathbf{J}_i$ as a function of the state parameters describing a non-equilibrium system is a good ground to attribute these flows to the state functions of such systems[1]. Note that this statement could by no means ensue from the existing theory of irreversible processes since this theory, according to the local equilibrium hypothesis, has never treated the thermodynamic forces as system state variables. Functional relationship (2.6.5) allows writing the exact differential of the flow $\mathbf{J}_i$ as:

$$d\mathbf{J}_i = \Sigma_i (\partial\mathbf{J}_i/\partial\Theta_i)d\Theta_i + \Sigma_j(\partial\mathbf{J}_i/\partial\mathbf{F}_j)d\mathbf{F}_j \; (j \neq i). \tag{2.6.6}$$

Now, to find the displacement flows, this expression should be integrated between the limits from the equilibrium state (where all $\mathbf{J}_i = 0$) to the current state:

$$\mathbf{J}_i = \Sigma_i \int(\partial\mathbf{J}_i/\partial\Theta_i)d\Theta_i + \Sigma_j\int (\partial\mathbf{J}_i/\partial\mathbf{F}_j)d\mathbf{F}_j \quad (j \neq i). \tag{2.6.7}$$

Note that the equilibrium state with $\mathbf{J}_i = 0$ is attained for the so-called "memory-possessing media" (viscoelastic and viscoplastic materials, hysteresis phenomena, etc.) generally at some the so-called "threshold" force value $\mathbf{F}_{j0}$ other than zero. Therefore the integration with respect to $\mathbf{F}_j$ will be started from exactly this value $\mathbf{F}_{j0}$. Taking into account the fact that the value of any parameter does not depend on the integration path, let us, for convenience's sake, integrate (2.6.7) first with respect to Θ_i at $\mathbf{F}_j - \mathbf{F}_{j0} = 0$ and then with respect to $\mathbf{F}_j$ at Θ_i = const. In this case the integral of the first sum in this expression does not at all contribute to the flow $\mathbf{J}_i$ since at equilibrium state ($\mathbf{F}_j - \mathbf{F}_{j0} = 0$) none of the coordinate Θ_i variations can cause

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[1] This statement is especially evident for isolated systems: all processes running therein are defined by exclusively the properties of a system as itself.

the flow $\mathbf{J}_i$. As for the terms of the second sum, they may be represented more compactly by designating

$$K_{ij} \equiv (\partial \mathbf{J}_i / \partial \mathbf{F}_j) \quad (j \neq i). \qquad (2.6.8)$$

Then expression (2.6.7) becomes:

$$\mathbf{J}_i = \Sigma_i \int K_{ij} \, d\mathbf{F}_j \, . \qquad (2.6.9)$$

Let us consider the most general case, when the phenomenological coefficients L_{ij} explicitly depend on the forces $\mathbf{F}_j$ and thermostatic variables Θ_j, i.e. $K_{ij} = K_{ij}(\Theta_j, \mathbf{F}_j)$, and. the dependence of $\mathbf{J}_i$ on $\mathbf{F}_j$ is non-linear. Then this relation may be represented in the pseudo-linear (linearized) form. Factoring some values of the functions $\overline{K}_{ij} = \overline{K}_{ij}\,(\Theta_j, \mathbf{F}_j)$ averaged between the limits from $\mathbf{F}_{j0}$ to $\mathbf{F}_j$ outside the integral sign the above expression becomes:

$$\mathbf{J}_i = \Sigma_i \, \overline{K}_{ij} \, (\mathbf{F}_j - \mathbf{F}_{j0}), \quad (i, j = 1, 2, ..., n_j) \qquad (2.6.10)$$

This expression is the most general form of the equations describing the transfer of heat, substance, charge, momentum, etc. In many of phenomena the threshold value $\mathbf{F}_{j0}$ of the force $\mathbf{F}_j$ may be neglected. Then the transfer laws in the form of 2.6.10 can be rewritten in a simpler form:

$$\mathbf{J}_i = \Sigma_i \, \overline{K}_{ij} \, \mathbf{F}_j \, . \qquad (2.6.11)$$

Thus thermokinetics suggests for an investigator a self-consistent form of representing the results of experiments on finding the transfer equations. As for the proportionality factors $\overline{K}_{ij}$ themselves, their finding is the problem for physical kinetics that uses for this, along with experiment, also considerations of the molecular-kinetic and statistical-mechanical theories.

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

Conclusions to Part 1

One of the most attractive features of the thermodynamic method has always consisted in its possibility to obtain, based on few primary principles ("the beginnings"), a great number of consequences covering various phenomena and having the status of oracles. Being consistently phenomenological (i.e. empirical), this method enables to reveal the general behavior of various processes without intruding into their molecular mechanism and not resorting to modeling on structure and composition of a system under investigation. All this contributed to the exclusive heuristic value and potency of the thermodynamic investigation method.

The intention to keep these advantages impelled us to base thermokinetics on the same methodological principles as a consistently phenomenological and deductive theory. The methodological concept of thermokinetics features not only the system approach to objects of investigation which became possible with introducing the parameters of their spatial heterogeneity, but also negation of process and system idealization, exclusion of postulates and hypotheses from the theory grounds, as well as the strictly deductive method used to obtain all its consequences. None of the other physical theories offers advantages in such a combination.

The body of mathematics thermokinetics operates is attractively simple and not outstepping the framework of college educational packages. Following the classic thermodynamic method of characteristic functions this body of mathematics is mainly based on the properties of their exact differential and "imports" all the rest data on the properties of a system under investigation "from outside" as uniqueness conditions of a kind. This imparts the status of oracles to the thermokinetics consequences providing the uniqueness conditions comply with the framework of experiment. It is naturally to expect, therefore, that the theory based on these principles will open up new vistas in cognition of Nature.

Part 2

HEAT ENGINEERING FUNDAMENTALS

The main object of this section is to give a methodologically unitary substantiation and statement of the principles, laws and equations for a number of fundamental disciplines constituting the theoretical grounds of heat engineering (the theory of heat engines, thermodynamics of reversible and irreversible physicochemical processes and the theory of heat-mass exchange). Such a statement paves the shortest way to comprehension and cognition of the above disciplines – the way free of multiple extraneous features these disciplines have historically acquired in the making. This way is based on a unitary notional system and further clarifies the interdisciplinary links facilitating the comprehension of their specificity, as well as the further in-depth study of the disciplines. At the same time such an approach excludes the necessity to extrapolate the notional and conceptual base of these disciplines beyond the rigorous frames of its own applicability thus facilitating the further critical analysis of the problems arising in various spheres these disciplines applcations.

Chapter 3

CLASSIC THERMODYNAMICS

Present-day thermodynamics has long outgrown the initial frames of the heat-engine theory and transmuted into a rather general macroscopic method for studying kinetics of various transfer processes in their inseparable connection with the thermal form of motion. However, it is still rooted in the conceptual system of equilibrium thermodynamics (thermostatics) remote from the transfer concept and in its body of mathematics going over into inequalities when considering real (non-static, irreversible) processes. Even in the current manuals on thermodynamics its construction quite often starts with describing the theory of ideal cycles and ideal gases as its working media. Such a "squared idealization" in the theory grounds themselves could not help creating problems in the further generalization of thermodynamics to systems differing from those idealized.

The escape from the situation may be found in obtaining basic statements of thermodynamics by deductive way as consequences of thermokinetics in order to avoid the extrapolation of classic thermodynamics beyond the framework strictly bounding the applicability of its initial concepts. This chapter is mainly dedicated to ascertaining the minimal scope of the corrections necessary to introduce into the fundamentals of thermodynamics from the positions of thermokinetics.

3.1. Principle of the Excluded Perpetuum Mobile of 1st Sort (the First Law of Thermodynamics)

R. Clausius, the founder of classic thermodynamics, presumed the principle of heat Q and work W equivalence generalizing the results of numerous experiments to be the only reliable basis to thermodynamics. He formulated this principle as follows, ”In all cases, when heat becomes work in a cyclic process, the amount of the heat expended is proportional to the work done and vice versa, work done is converted into an equivalent amount of heat” (Clausius, 1876). If heat and work are measured in the same units of the international system of units, SI, the equivalence principle may be written as a simple relationship:

$$Q_c/W_c = 1, \tag{3.1.1}$$

or

$$\oint (đQ + đW) = 0 \tag{3.1.2}$$

where $đQ$, $đW$ – elementary amounts of heat and work for particular parts of the cyclic process under consideration.

Clausius was the first who noticed that the above relationship did not depend on the nature of the cyclic process under consideration. According to a known curvilinear integral theorem the fact the integral along the contour within the space of variables x_1, x_2,... x_n becomes zero is a sufficient evidence that the integrand represents the exact differential of some function of these variables $U(x_1, x_2,..., x_n)$.

Thus the principle of equivalence meant the existence of a specific function of state U, which variation was equal to the algebraic sum of heat and work of a process. Allowing for the rule of signs accepted in thermodynamics (the heat Q fed into a system and the work W done by the system being positive), the integrand may be expresses as:

$$dU = đQ - đW . \tag{3.1.3}$$

R. Clausius named the function *U the total heat of a body* (he meant the sum of the heat *Q* fed into a system and the "disgregation" work of the dissipative nature, which replenished the "heat of the body" – the energy associated with heat motion in the system). Such an understanding reflected a known duality of the heat concept, which had historically been caused by consideration of the heat as a form of motion (in the same line with such phenomena as light, sound, electricity, magnetism). This duality means that heat shows in some cases as the state function (heat of a body), whereas in other cases – as the process function (heat of a process). Therefore from Clausius' times on the function *U* has been referred to as the *internal energy* of a system. However, despite plenty discussions the said duality in using the term "heat" survives to this day. Accepting this fact as a historically preconceived reality, let us name the internal heat energy, for short, the "heat of a body", whereas the quantitative measure of heat transfer – the "heat of a process" designating, for the avoidance of mishmash, the former through U_q and the latter through Q. In this case, to designate the infinitesimal increments of internal heat energy as a function of state, let us use the sign of exact differential d, whereas to designate the elementary amount of work W or heat Q as a process function – the sign $đ$ ($đW, đQ$).

Equation (3.1.3) has been named the *first law of thermodynamics.* This reflects the constancy of energy of an isolated system (U = const at Q, W = 0) and therefore is one of the statements of the *law of conservation of energy.* This law reflects the conservation of the internal energy U at its interchange among a system and the environment in the form of heat Q or work W. With regard to a cyclic process (cycle) expression (3.1.3) may be written as:

$$\oint đQ = \oint dU + \oint đW \quad \text{или} \quad Q_c = \oint dU + W_c, \tag{3.1.4}$$

where Q_c, W_c – total heat and work of the cyclic process.

Since the circuit integral of any state parameter, including the system energy U, is equal to zero, expression (3.1.4) directly gives that $W_c = Q_c$, i.e. the work done by working medium for a cycle is equal to the heat it expendes in the cycle. In other words, *a cyclic machine is impossible, which would do work without heat expenditure.* This statement was named the *law of excluded perpetual motion of the first kind.*

At its early stages classic thermodynamics was restricted to the simplest thermo-mechanical systems, where expansion work was the only kind of work. A system having been in equilibrium with the environment (equal pressures p), that work was determined from mechanical interpretation of pressure as a force and expressed by the relationship $đW_p = pdV$, where V –

volume of the system. From there the so-called analytical expression for the first law of classic thermodynamics ensued in the form:

$$đQ = dU + pdV. \qquad (3.1.5)$$

It may be said without exaggeration that the majority of methodological features intrinsic for thermodynamics, as well as its insufficiency, is caused by that specific form (3.1.5), in which it involves the law of conservation of energy. Expression (3.1.5) first of all involves only two forms of power interchange in a system, viz. heat Q and work W done by the equilibrium system[1)]. Meanwhile, one more type of power interchange referred to neither heat transfer nor work take place in a great number of cases of practical interest. This is mass transfer associated with the k^{th}-substances interchange between a system and the environment. Such systems are called open ones. These types of power interchange are not covered by equation (3.1.5) describing the law of conservation of energy, therefore the principle of equivalency of heat and work can not serve as a basis for further generalization of this law to open systems. To do this, a more general approach is needed, which is exactly what thermokinetics puts forward.

Furthermore, equation (3.1.3), unlike (2.2.5), does not contain any forces $\mathbf{X}_i$ causing the generation of the energy-conversion processes. Its terms on the right-hand side characterize energy interchange between a system and the environment in the form of heat and cubic strain work (confirming the principle that a system can only exchange what it really has). Therefore it describes only processes of energy *transfer*, but not *conversion.* In other words, the first law of thermodynamics characterizes the balance of energy only and has nothing to do with the law of conservation of energy at its conversion. It is even more true, because an internally equilibrium (homogeneous) system can not do useful work in the absence of other bodies (environment), with which it is not being in equilibrium. Besides, the energy balance itself described by equation (3.1.5) comes valid provided the system being in equilibrium with the environment. Actually, in the absence of, e.g., mechanical equilibrium between a system and the environment (when the pressure p in the system is not equal to the environmental pressure p_e, and the expression pdV does not define the expansion work any more) the analytical expression of the first law of thermodynamics (3.1.5) goes over into inequality:

$$đQ \neq dU + pdV\,. \qquad (3.1.6)$$

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1) Such work will hereafter be referred to as “non-technical” unlike the useful external (technical) work done by various machines (by extended systems).

This is the reason why the first law in the form (3.1.5) is valid for only completely (both internally and externally) equilibrium systems.

One more reason of the insufficiency classic thermodynamics demonstrates is caused, strange though it may appear, by the notion of internal energy as itself. energy *U* belonging to, strictly speaking, entire set of the interacting (relatively moving) bodies is known to be far from being possibly attributed to one of the comprising parts considered as the object of investigation. This may be done to only that part which does not depend on position and motion of the system relative to other bodies and is defined by exclusively parameters of the system itself. That is exactly where the definition of the *internal energy U* is rooted in. However, it ensues from this definition that such a system can not do useful external work measured by the variation of external potential or kinetic energy of a system of interacting bodies. Therefore the internal energy of an equilibrium system is actually the *anergy* (see Chapter 2).

The notion of internal energy is quite often extrapolated to systems lying in external fields of forces, which are, e.g., dielectric and magnetic materials. Their energy is known to be dependent on not only internal variables, but as well on intensities of these fields. However, these are often associated with the notion of magnetic and dielectric "internal self-energy" considering it sufficient to subtract the energy of electrical and magnetic fields from the total energy in the volume occupied with the system. This makes thermokinetics consider a polarized medium along with a polarizing field as a whole and, generally, non-equilibrium system. Such an approach is substantiated by the fact that an attempt to isolate a dielectric or magnetic field from the surrounding fields of forces leads to change of their state (relaxation), which excludes a possibility of treating their energy as internal one (self-energy) and applying equation (3.1.3) to it.

There are also other serious and yet hardly perceived constraints for the equations operating with the notion of internal energy. In this sense the term "thermodynamic" may be applied only to the so-called "simple" media, where long-range and surface forces may be neglected since their energy can not be attributed to just one of the interacting bodies (Caratheodory, 1964). From this one more constraint ensues, viz. for size of a system. This exists not only "from above" (for galactic-size systems where long-range gravitational forces can not be neglected), but also "from below", e.g., for usual continuums since when artificially splitting them into elementarily small zones the surface energy of the continuum elements increases and may appear non-negligible (Putilov, 1971; Bazarov, 1983).

To exclude all these constraints, thermokinetics considers as the object of investigation "extended systems" comprising such a set of interacting (relatively moving) bodies and fields, which energy, to enough degree of accuracy, may be considered as its "self-energy". Such systems may be isolated not disturbing their internal state and energy. Furthermore, thermokinetics offers an absolutely other (and in many ways oppositional) approach to stating the law of conservation of energy. This approach is notable for its basing the law of conservation not on the energy balance equation, which equation (3.1.3) is, but on the representation of the system energy as a function of a quite definite number of the system state parameters.

Suppose we deal with a thermo-mechanical system having only two (thermal and mechanical) degrees of freedom. These two degrees of freedom are described with two extensive state coordinates, which we formally designate as Θ_t and Θ_e. Their meaning will be explained hereafter. For now it is enough to know that the total energy of the system (consisting in this case exclusively of its internal energy U) as a function of state is expressed in the form of $U = U(\Theta_t, \Theta_p)$, whereas its exact differential may be written as:

$$dU = (\partial U/\partial\Theta_t)d\Theta_t + (\partial U/\partial\Theta_e)d\Theta_e\,. \tag{3.1.7}$$

Designating $\Psi_t \equiv (\partial U/\partial\Theta_t)$ и $\Psi_e \equiv (\partial U/\partial\Theta_e)$ gives a thermo-dynamic identity:

$$dU \equiv \Psi_t d\Theta_t + \Psi_p d\Theta_p\,. \tag{3.1.8}$$

According to this identity the energy of the system varies with variation of the said parameters Θ_t and Θ_e irrespective of what causes the variation – either energy interchange or internal processes in the system. Undoubtedly, in the latter case the terms $\Psi_t d\Theta_t$ and $\Psi_e d\Theta_e$ do not reflect any more heat exchange or cubic strain work. To define them, thermokinetics offers other ways (see Chapter 2). That enabled thermokinetics to refuse the classification of processes by the type of energy interchange. It was the said classification that engendered the problem of thermodynamic inequalities. As a matter of fact, the principle of classification by the type of energy interchange demands the availability of state coordinates that would remain unvaried in the absence of heat transfer processes and expansion work. However, this is excluded in a non-equilibrium system, where a number of its parameters can vary spontaneously. For this reason classic thermodynamics is known to be restricted to equilibrium states and quasi-static processes not practically disturbing this equilibrium.

Unlike it, thermokinetics classifies processes by exclusively those state variations they cause. Such a classification provides the fundamental equation of equilibrium thermodynamics in the form of (3.1.7) retains the nature of identity even in the case when the parameters Θ_t and Θ_p vary spontaneously, i.e. in the whole range of real processes.

3.2. Principle of Entropy Existence (Second Law for Reversible Processes)

Let us clarify the meaning of the variables Θ_t and Θ_e introduced above formally (by definition). Let us start off with the coordinate Θ_e of expansion work. It is considered quite natural to accept for this the volume V of a system. However, in this case the volume-correlated system potential $\Psi_e \equiv (\partial U/\partial V)$ according to relationship (2.2.2) takes on the meaning of pressure reversed in sign ($\Psi_p \equiv - p$). According to equation (2.3.2) this entails opposite-to-actual sign of the motive force of gas flow transfer process (as known from experience, gas flow is transferred by pressure-gradient force toward the lower-pressure zone – just like with potentials of other nature). Furthermore, the volume (positive or negative) does not comply with the requirement of thermokinetics for potential and coordinate of some process simultaneously becoming zero. Lastly, the volume of a system can not serve as a cubic strain coordinate in open systems because it necessarily varies at mass transfer with the density ρ of the system remaining constant. For systems, where the processes of composition variation run (due to diffusion of the k^{th} substances across the borders of the system at constant mass M of the system), the cubic strain coordinate issue grows even more complicated since the system density $\rho = \Sigma\, c_k\rho_k$ can vary with constant density ρ_k of any of the k^{th} substances, but with the variation of the fractions c_k of their total masses. Therefore the cubic strain issue appears to be, in actual fact, not that plain.

From thermokinetics any state coordinate Θ_i is considered as a quantitative measure of the corresponding form of energy in a system and therefore increases with increase of this energy. If, for the sake of simplicity, to be confined to only closed systems (M = const) of a constant composition (c_k = const), this demand is met by the difference between the theoretical compression limit $V_o = 0$ (this is the state corresponding to zero of the cubic strain coordinate Θ_e) and the current value of the volume V, i.e.

$$\Theta_p = (V_o - V). \qquad (3.2.1)$$

It is easy to see that Θ_e complies with all requirements for the cubic strain coordinate. In particular, $d\Theta_e = - dV$, and

$$\Psi_p \equiv (\partial U/\partial \Theta_p) = - (\partial U/\partial V) = p. \qquad (3.2.2)$$

which provides further the concordance of signs for all potentials and forces of a system.

In equilibrium systems, where the reversible expansion work done by a system is the only reason of changing the volume of the system, according to (3.2.1) $đW_p = pdV$, which corresponds to expression (3.1.4). In more general case of non-equilibrium systems the term pdV characterizes the process of uniform compression or expansion of a system (its uniform cubic strain) irrespective of what causes it – either the compression (expansion) work done by the system or the energy dissipation (including that from overcoming frictional forces or from spontaneous expansion into void).

The next challenge R. Clausius, the founder of thermodynamics, faced on the way to representing the law of conservation of energy (3.1.3) in terms of state parameters was to find the heat transfer coordinate as a value remaining unvaried in adiabatic processes. R. Clausius found that coordinate thru splitting the arbitrary cycle of the heat engine by series of adiabatic and isothermal lines into a number of elementary reversible Carnot cycles. Designating the elementary amounts of heat being received and delivered in such elementary cycle at temperatures T' and T'', respectively, thru $đQ'$ и $đQ''$ gives the following form of the thermal efficiency η_t for each of such cycles:

$$\eta_t \equiv 1 - đQ''/đQ' = 1 - T''/T' . \qquad (3.2.3)$$

From this it follows that the sum $đQ'/T' + đQ''/T''$ of the so-called "reduced heats" $đQ'/T'$ and $đQ''/T''$ is equal to zero over all elementary cycles, i.e. the circuit integral, in its limit, of the reduced heat

$$\oint đQ/T = 0 \qquad (3.2.4)$$

appears to be equal to zero irrespective of the cycle configuration. This means that the integrand $đQ/T$ is the exact differential of some function of state, which Clausius named the entropy:

$$dS = đQ/T \text{ или } đQ = TdS. \qquad (3.2.5)$$

It was thereby proved the existence of a reversible process coordinate, i.e. a state parameter which variation is a necessary and sufficient criterion of running the heat transfer process. That statement R. Clausius referred to the second law of thermodynamics as the law of entropy. The further investigations (T.A. Afanasieva–Erenfest, 1928; A.A. Guhman, 1947; N. Petrov, J. Brankov, 1986) have shown that the law of entropy comprises two quite independent statements referred to, respectively, reversible and irreversible processes, viz. the laws of existence and increase of entropy. With all this going on, relationship (3.2.4) being the mathematical expression of the second law of thermodynamics for reversible processes has been proposed as the law of existence of entropy (A.A. Guhman, 1947).

With the lapse of time the concept of entropy has crossed the borders of not only thermodynamics, but also physics, and penetrated into the inmost of human brain. Therefore, many investigators have remained unsatisfied with the close connection between the concept of entropy and Carnot ideal gas cycles. Other ways have been tried for a long time to substantiate existence of entropy. The Caratheodory's system (Caratheodory, 1909) is commonly considered as the mathematically strictest and logically most consistent of all others. C. Caratheodory based his substantiation of existence of entropy and absolute temperature on an "axiom of adiabatic unattainability", according to which "in any vicinity of the initial state arbitrarily prescribed there are such ones which can not be however accurately approximated by adiabatic state variations". The implication of this axiom is most distinct from the Afanasieva–Erenfest's (1928) statement, "Provided $\text{đ}Q = 0$ on infinitesimal way between two infinitely close states of a thermally homogeneous system, then none of mere adiabatic quasi-static ways is possible as bypass between these states". The "bare root" of the Caratheodory's axiom is thus growing from the evident ground that *reversible heat exchange results in such variations of state which can not be attained by any other way as well reversible.* It is easy to see that this statement is a particular case of the *process distinguishability principle (axiom)* we have embedded into the foundation of the process classification (Chapter 2). This axiom, as applied to heat exchange process, just logically results in a statement that a parameter exists, which variations reflect those specific state changes distinguishable in kind and non-reducible to each others, which the reversible heat exchange causes. However, Caratheodory was persistent in his intent to prove the existence of entropy not recurring to notions of non-mechanical nature (in particular, to the notions of heat and temperature). That was what engendered a known complexity and awkwardness of his entropy-existence substantiation. The main point of his approach offered consists in proving the holonomy of the expression $\text{đ}Q = dU + pdV$, i.e. that this the so-called "Pfaffian" form contains the integrating factor 1/T converting the heat element $\text{đ}Q$ into the exact differential of some function of state, which Clausius has earlier named entropy. The fact is that the heat $\text{đ}Q$ and the work $\text{đ}W$ elements as themselves in the equation (3.1.3) of the first law of thermodynamics are not exact differentials since their values depend on the nature of a process. In particular, for adiabatic processes $\text{đ}Q = 0$, for isochoric ones $\text{đ}W = 0$. That is what required the representation of the elementary heat in terms of the exact differential of some function of state, i.e. per se the determination of the heat exchange coordinate.

As we'll try to show hereafter, the one can avoid this complexity who classifies processes not by the energy exchange type, but by those specific state variations the processes cause. In this case it should be admitted a specific process exists dependable on a change of the system internal heat energy irrespective of what causes this change, either the external heat exchange Q or internal sources of the dissipative heat Q^{d} (from friction, chemical transformations, high-frequency or induction heating, etc[1]). Let us name this process, after K. Putilov (1971), the *thermal process.* Then it directly ensues from the theorem of degrees of freedom proven in Chapter 1 that a specific coordinate of the said process exists designated as Θ_t in the previous chapter. All we have to do now is to clarify the relationship between the thermal process coordinate and the heat exchange coordinate, viz. the Clausius' entropy S. With this purpose let us use the equilibrium conditions determination method, which idea belongs to J. Gibbs (1885). Let us consider the conditions, at which the thermal equilibrium occurs between two parts (subsystems) of a system isolated in whole. The subsystems have intrinsically different empirical temperatures τ' and τ'' and are separated with a rigid diathermic (thermo-penetrable) partition. Since during the process of equilibrium setting the energy of such a system remains unvaried, the equilibrium condition according to equation (3.1.4) is expressed as the absence of the energy variation $đU$ for the system as a whole at any energy variations $\delta U'$ and $\delta U''$ for the subsystems (which is caused by the dynamic nature of thermal equilibrium):

$$\delta U = \delta U' + \delta U'' = \Psi_t' d\Theta_t' + \Psi_t'' d\Theta_t'' = 0. \tag{3.2.6}$$

Taking into account that in the thermal equilibrium state there are no any internal sources for the Θ_t' and Θ_t'' coordinates, while the system as a whole is isolated (Θ_t = const), gives that possible variations Θ_t' and Θ_t'' in the subsystems obey the evident constraint:

$$\delta\Theta_t = \delta\Theta_t' + \delta\Theta_t'' = 0. \tag{3.2.7}$$

Considering (3.2.6) jointly with equation (3.2.7) of imposed constraints may lead to a conclusion that at thermal equilibrium the equality of potentials Ψ_t' and Ψ_t'' in both subsystems takes place:

$$\Psi_t' = \Psi_t''. \tag{3.2.8}$$

It is known from experience that thermal equilibrium is reached under equality of the empirical temperatures τ' and τ'' in subsystems measured in an arbitrary temperature scale (Celsius, Réaumur, Fahrenheit, etc.). Hence, the potentials Ψ_t' and Ψ_t'' are some functions of these temperatures, i.e. $\Psi_T' =$

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[1] Note that from the positions of equilibrium thermodynamics, where heat has been construed as a function of process, it would be incorrectly to qualify the "heat of a body" as a quantitative measure of the internal heat energy U_t. However, in thermokinetics, like in thermal physics, the heat exchange is construed as a process of exchanging the internal heat energy U_t among bodies (confirming the principle that a system can only exchange what it really has). This considerably facilitates the comprehension of thermal process specificity.

$\Psi_t'(\tau')$; $\Psi_t'' = \Psi_t''(\tau'')$. Since this statement is a generality and does not depend on the kind of substances in subsystems, the above functional dependence must be unified for all substances (*universal*) [1]. Furthermore, equality (4.2.7) is valid *as long as heat exchange between subsystems is possible*, i.e. until the heat motion in subsystems caused the particular type of energy exchange has ceased. From this it follows that the temperatures τ' and τ'' differ from zero *as long as heat exchange exists between any cogitable bodies*. This means that the potentials Ψ_t' and Ψ_t'' must be measured in the so-called absolute temperature scale, which zero *corresponds to the total degeneracy (disappearance) of heat motion.* It is the Kelvin scale that is known to meet these requirements. Designating the temperature in this scale thru T leads to a conclusion that the variation of the thermal process coordinate Θ_t in equilibrium systems is related to heat exchange via the same relationship as the Clausius' entropy:

$$d\Theta_t = đQ/T = dS\,. \tag{3.2.9}$$

From this it follows that the thermal process coordinate Θ_t coincides with the Clausius' entropy S to an accuracy of some constant (which may be set zero, though). This allows expressing thermodynamic identity (3.1.7) thru informal variables:

$$dU \equiv TdS - pdV. \tag{3.2.10}$$

Fundamental difference of this identity from the joint equation of the first and second laws of thermodynamics, where unequal sign figures instead of identity sign (for irreversible processes), lies in the fact that the former remains valid for also irreversible processes. Undoubtedly, in this case the terms of this identity do not characterize any more heat exchange and expansion work as it would be for reversible processes. The reason of this, as indicated above, is that entropy and volume have internal sources caused by dissipative processes running in heterogeneous systems. The variations of volume and entropy are, in this case, caused by not only the expansion work and the heat exchange, but by even more general processes, viz. cubic strain and thermal process both including an irreversible component. Such is the price that has to be paid for retaining the body of mathematics in thermodynamics in the form of equalities.

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[1] This chain of discourse makes quite evident the necessity to measure in absolute scale not only temperature, but also pressure, chemical, electrical and any other potential of a system under investigation._ It is a matter for regret that this statement has not yet become common property of a great number of investigators.

3.3. Principle of Entropy Rise (Second Law for Irreversible Processes)

In accordance with the law of existence of entropy the entropy means a state parameter, which variation in reversible processes is equal to the process heat Q related to the process average temperature T. However, the name of this parameter given by R. Clausius (entropy in Greek means "internal conversion") emphasized a quite other and unusual for science of that time property of entropy to increase also in the absence of heat exchange (due to a spontaneous conversion of ordered forms of energy into the heat energy). 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).

Since all known thermodynamic systems being isolated are tending to equilibrium (where any macro-processes cease), the capability of such systems to do work decreases when spontaneous processes are running. To describe such a behavior mathematically, R. Clausius considered two "mating" heat engines – one engine working by direct cycle, while the other – by reverse cycle. He took for granted that the thermal efficiency η_t of any irreversible heat engine was less than in the reverse Carnot cycle (at the same temperatures of heat absorber and heat source). If so, then the equal sign in relationship (4.2.3) must be replaced by the unequal sign:

$$\eta_t \equiv 1 - \text{đ}Q''/\text{đ}Q' < \eta_t^{\mathrm{K}} = 1 - T''/ T' . \qquad (3.3.1)$$

In this case, repeating the same operations we immediately come to a conclusion that entropy of a system increases if any irreversible processes are running in the system:

$$dS > \text{đ}Q/T, \qquad (3.3.2)$$

Thus the law of increase of entropy appeared. It reflects the unilateral directivity of spontaneous processes and has acquired the status of the second law of thermodynamics. According to this law the entropy of an isolated system increases when any irreversible processes are running in it. R. Clausius, not having conceived restrictions to this law, extended it to the entire Universe. Such "absolutization" of the law of increase of entropy is best of all highlighted in his winged words, "The energy of the Universe is invariable. The entropy of the Universe is increasing".

Clausius's contemporaries immediately traced far-reaching effects in that conclusion – from "the Creation" up to inevitability of "heat death" of the Universe. A good few of investigators even at that time treated such an extrapolation of the law of increase of entropy as extremely unconvincing (J.M. Gelfer, 1979). It is impossible to textually duplicate here even the least of the objections ensued. Under these circumstances the deduction of the law of increase of entropy from the positions of thermokinetics is a matter of great interest. The definition of the internal heat energy $U_{\text{т}}$ given above makes quite natural and predictable its increase not only due to the heat exchange Q, but also due to internal sources of the dissipation heat Q^{D}:

$$dU_{\text{т}} = \text{đ}Q + \text{đ}Q^{\text{д}}. \qquad (3.3.3)$$

Since the quotient obtained when the exact differential of any function of state (in this case – of U_t) is divided by any parameter Ψ_{t} (in this case – by absolute temperature T) is also the exact differential, the expression $d\Theta_{\text{т}} = dU_t/T$ does not demand the proof of holonomy and directly leads to the entropy balance equation I. Prigogine (1947) set forth:

$$dS = d_eS + d_uS\ . \qquad (3.3.4)$$

Here $d_eS = \text{đ}Q/T \leq \geq 0$ – reversible part of the entropy variation caused by the external heat exchange $\text{đ}Q$; $d_uS = \text{đ}Q^d/T \geq 0$ – irreversible part of the entropy variation caused by internal sources of the dissipation heat $Q^d \geq 0$. Under this expression the entropy S of adiabatically isolated systems (where $\text{đ}Q = 0$) increases when any internal sources of the dissipation heat appear in them.

At the same time expressions (3.3.2) and (3.3.3) manifest clearly the inapplicability of the law of increase of entropy to irreversible processes, where the work counter the dissipation forces affects other components of the internal energy and does not initiate internal sources of the dissipation heat Q^d. In particular, metal cutting and material crushing processes involve changing the internal potential energy depending on the system structure. This is estimated in practice by the heat output ratio which is the dissipation heat Q^d related to the work expended W. For many processes the ratio Q^d/W is less than unit. Thus, from the positions of thermokinetics, it becomes absolutely evident that the thermodynamic entropy is not a measure of "each and either" irreversibility, but just reflects the fact of increasing the internal heat energy at the expense of other "non-entropy" forms of energy. The understanding of this circumstance is considerably facilitated by comparing the exact differential of the internal heat energy (4.3.3) $dU_t = TdS$ with the similar expression for the kinetic energy $dE^k = \mathbf{v}d\mathbf{P}$ (where **v** – velocity of a system, **P** – its momentum):

$$dU_{\mathrm{T}} = TdS\,;\; dE^k = \mathbf{v}\cdot d\mathbf{P}\,. \qquad (3.3.5)$$

It is easy to notice that the entropy S behaves toward the internal heat energy U_t of a system in the same way as the momentum **P** of the system toward its kinetic energy. In other words, *the entropy of a system is a thermo-momentum of a kind, i.e. the sum of momentum magnitudes of the particles comprising the system, which has lost its vector nature due to the randomness of heat motion.* It is natural therefore that the entropy as a thermo-momentum of a system increases not only at its transfer from the environment during heat exchange with the same, but at any dissipation processes involving the conversion of ordered forms of energy into the internal heat energy. The interpretation of the entropy as a thermo-momentum is a matter of no small consequence for conception of thermodynamics and its further generalizations. In particular, it becomes evident that the thermodynamic entropy can not serve as measure of the disorder not relating to heat motion, including the disorder of structure or uncertainty of information. In this respect the conversion of the *ynergy* of a system into its *anergy* (see chapters 7, 8 and 14) is a much more general criterion of an isolated system evolving toward equilibrium. Such a conversion has an experimental confirmation, which may be, e.g. the so-called "effect of increasing heat content measured" (L. Brovkin, 1960, 1964). Those experiments revealed an increase of the mean integral temperature during the relaxation of gaseous or solid medium (paper, cardboard, rubber) with heterogeneous temperature field, whereas that temperature should seemingly have decreased. Characteristic are herein the experiments with a roll of paper, where throughout the length a resistance thermometer was inserted. After the tightly packed roll had been non-uniformly heated from an external source of heat, the system was lagged (heat insulated) and the resistance variation of such a "spread" thermometer was recorded. Series of such experiments revealed a considerable increase of the mean integral temperature of the roll for the initial period of its "cooling", which amounted to 17.2% thru 36.4% depending on the degree of its heating. For rubber that effect appeared to have been even higher. That unambiguously evidenced the fact that the equilibrium component of the internal heat energy of the body (its anergy) $\bar{U}_t = TS$ increased whereas the U_t itself remained constant, i.e. that the thermal ynergy existed and transformed into the anergy during the relaxation of the system. Hereafter we will time after time advert to the concept of inergy as more "physic", more informative and more general criterion of evolution that entropy.

3.4. Principle of Excluded Perpetual Motion of the Second Kind

Operation experience on heat engines and their theoretical investigation have led to the comprehension that there should exist in them, along with a heat source, also a heat absorber (or, to use the common locution – a "cold source"). Scientists have come to this conclusion by different ways: S. Carnot (1824) – from analogy of heat engines with hydraulic engines using the inlet-outlet water level differential; W. Thomson (1847) – from impossibility for working medium to be cooled below the ambient temperature; R. Clausius (1850) – from necessity of the "compensation" for converting heat into work as partial removal of this heat to surrounding bodies; W. Ostwald (1901) – from impossibility of using inexhaustible heat supply from the ocean. It was him, who offered to name engines lacking heat absorber the "perpetual motion of the second kind" (unlike the "perpetual motion of the first kind" lacking heat source and thus disturbing the first law of thermodynamics). The postulates stating impossibility of creating such engines make up an inseparable part of the second law of thermodynamics and are united by the "law of excluded perpetual motion of the second kind".

However, the initial statements of this law referred to cyclic heat engines only and did not take into account the wide process variety of converting energy from one form into another. Therefore to many investigators the consideration of non-cyclic and non-heat engines has always seemed violating the "don'ts" of the mechanical theory for heat engines. This causes numerous discussions that have periodically arisen in scientific and popular press. In this context it is a matter of interest to clarify the limits of validity of the said postulates from the positions of a more general theory which thermokinetics is.

Let us consider a heat source with a temperature of T_1 capable of heat exchange with the environment, but incapable of ceaseless mechanical work. In this case, to do work, a working medium has to be applied to capable of both heat-exchange and work, i.e. having both the thermal and mechanical degree of freedom. To avoid expenditure of working medium, let us make it perform a cyclic process (Fig.3-1). Providing such a working medium (e.g. steam or gas) is homogeneous in its physical properties (internally equilibrium), while the processes comprising the cycle are quasi-static (i.e. not disturbing this equilibrium), the joint equation of the first and second laws of thermokinetics (2.2.5) becomes (3.1.5). According to (3.1.4) the work W_c of such a cycle is equal to the heat of the cycle:

$$W_c = Q_c = \oint TdS. \qquad (3.4.1)$$

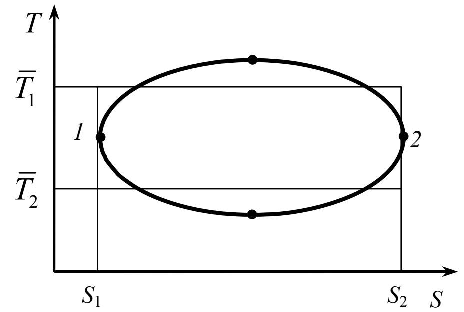

Fig.3.1. Generalized Cycle of Heat Engine

From this equation it follows that the work W_c in the cyclic process under consideration is other than zero only in the case, when the temperature T at various stages of the cycle accepts different values. Otherwise, factoring it outside the integral sign (3.4.1) and taking into account that the circuit integral of entropy, like of any state parameter, is equal to zero, gives immediately W_c=0. Thus working medium in a cyclic engine must periodically contact with at least two heat sources having different temperatures T_1 and T_2. In other words, both a "hot" and a "cold" heat sources are needed. However, it does not mean at all that the working medium can not take heat from both of them. To show that the cold source must be a heat absorber, let us note there is part 1–2 in the cycle, where the entropy increases and the heat $Q_1 = \int T_1 dS > 0$, i.e. is supplied to the working medium, and part 2–1, where the entropy decreases and the heat Q_2 is removed ($Q_2 = \int T_2 dS < 0$). Thus to run a cyclic process, both heat sources and absorbers are needed, which conceptualizes the law of excluded perpetual motion of the second kind. It is worth noting that this statement, as itself, directly ensues from the thermokinetic identity in the form of (2.2.5), where the terms of the addend sum characterize nothing but the useful work done by the system. These terms are structured as $\mathbf{X}_i \cdot d\mathbf{Z}_i$, which is a direct evidence that only heterogeneous systems ($\mathbf{X}_i \neq 0$) can do useful work, while this work itself involves transfer of energy carrier between the parts of such a system ($d\mathbf{Z}_i \neq 0$).

Following the chain of our discourse one can easily come to a concept of the degree of convertibility of heat into work. If to construe Q_1 and Q_2 as the heat, respectively supplied to and removed from the cycle, then according to (3.4.1) the work of an arbitrary cycle $W_\mathrm{c} = Q_1 - Q_2$ and is expressed by the cyclic area, while the ratio η_t of the cyclic work W_c to the heat Q_1 supplied from a hot source is:

$$\eta_t \equiv W_\text{ц}/Q_1 = 1 - Q_2/Q_1 < 1. \qquad (3.4.2)$$

This ratio was named the thermal efficiency of heat engine. According to (3.4.2) it is always less than unit. This fact is sometimes erroneously ascribed to shortcomings of heat engine leaving out of account the circumstance that removing a part Q_2 of the supplied heat Q_1 to the environment is not a loss, but the necessary provision to close the cycle. Only that part Q_2 may be considered as losses, which is removed to heat absorber in excess of the minimum required. To define this minimum, let us represent Q_1 and Q_2 as:

$$Q_1 = \int T_1 dS_{1\text{-}2} = \overline{T}_1 (S_2 - S_1); \qquad (3.4.3)$$

$$Q_2 = \int T_2 dS_{2\text{-}1} = \overline{T}_2 (S_1 - S_2), \qquad (3.4.4)$$

where $\overline{T}_1, \overline{T}_2$ – the so-called mean thermodynamic temperatures of, respectively, heat supply and heat removal in a cycle. In Fig.3-1 those are expressed as the height of a rectangle equal in area to, respectively, the curvilinear trapeziums S_1–1–2– S_2 and S_1–2–1–S_2. This allows expressing the efficiency of any cycle thru these temperatures by the relationship:

$$\eta_t = 1 - \overline{T}_2 / \overline{T}_1 < 1. \qquad (3.4.5)$$

From here it directly follows that the efficiency of the cycle under consideration will be maximal providing the temperatures of heat supplied and removed are constant and equal to, respectively, maximal and minimal temperature of the working medium in Fig.3.1. Such a cycle consisting of two isotherms and two adiabats was first set forth by *S*. Carnot and named after him. The removed heat Q_2 is there minimal and equal to Q_2^{min}. Hence only the heat difference $Q_2 – Q_2^{min}$ may be referred to as losses. It also ensues from (3.4.5) that the thermal efficiency of heat engine is defined by exclusively mean temperatures of heat supplied and removed in a cycle and, providing those are equal, does not depend on the working medium of the engine1). This statement is in substance equivalent to the Carnot theorem which he proved from the theory of thermogen and the assumption of reversibility (ideality) of his cycle. In our case we have come to all these statements without any assumptions regarding the cycle configuration and equilibrium of the processes comprising the cycle. From our consideration

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1) This fact means that the value of η_t does not depend on features of heat engine and its design perfection, but is defined by exclusively those resources that nature provides for the human, including the temperatures of heat source and heat absorber. Therefore some investigators have reasonably proposed to name η_t not “efficiency”, but “degree of reversibility” of the heat supplied.

undertaken it also follows that the "compensation" for the Clausius-mentioned conversion of heat into work consists in removing the heat Q_2 into the environment (heat absorber) and in increasing its entropy by the value ($S_2 - S_1$) theoretically equal to the decrease of the entropy of the heat source. In other words, to provide the heat conversion process, it is necessary to arrange a flow of entropy from the hot source to the cold one like the water flow in hydraulic engines. Yet S. Carnot noted this analogy between heat and hydraulic engines. Looking now back one can not choose but regret that after the theory of thermogen as the "indestructible fluid" failed this term has never been used to describe the carrier of the heat form of motion.

3.5. Principle of Unattainable Absolute Temperature Zero (Third Law of Thermodynamics)

This fact means that the value of η_t does not depend on features of heat engine and its design perfection, but is defined by exclusively those resources that nature provides for the human, including the temperatures of heat source and heat absorber. Therefore some investigators have reasonably proposed to name η_t not "efficiency", but "degree of reversibility" of the heat supplied.

Thorough investigation tests on substances to study their low-temperature behavior were undertaken in the early 20th century. As a result of these studies it has been found (W. Nernst, 1929) that on approaching the absolute temperature zero *the entropy of any equilibrium system in isothermal processes ceases to depend on whatever thermodynamic state parameters Θ_i and in its limit at $T=0$ accepts a value the same for all system, which may be taken zero* (I.P. Bazarov, 1991). This is mathematically expressed by the relationship:

$$\lim_{T\to 0} (\partial S/\partial \Theta_i)_T = 0. \qquad (3.5.1)$$

The validity of this statement named the third law of thermodynamics is presently substantiated for all equilibrium systems. Apparent deviation from this law revealed for some substances (glycerol, CO, NO, some alloys) appeared to have been attributed to a "freezing" of them in a meta-stable non-equilibrium state that passed off in some (sometimes very long) time.

Practical value of the third law consists in its advanced facilitation of calculating the thermodynamic functions. Before that law stated, to calculate entropy, it was necessary to know the dependence of heat capacity on temperature and the thermal state equation. Now this has become needless, since according to the heat capacity definition

$$C_v = T(\partial S/\partial T)_V ; \; C_p = T(\partial S/\partial T)_P \qquad (3.5.2)$$

integration of these equations gives:

$$S(T,V) = \int (C_v/T)dT ; \; S(T,p) = \int (C_P/T)dT , \qquad (3.5.3)$$

where the integration is performed from the absolute temperature zero. Since according to the third law the entropy is finite at any temperature, the integrals (3.5.3) must be converging. From this it follows that the isochoric and isobaric heat capacities at $T \rightarrow 0$ tend to zero faster than the temperature (Einstein, 1966).

The availability of relationships (3.5.3) substantially facilitates calculating the entropy of bodies, when the dependence of their heat capacity on temperature is known.

At the same time the third law is a matter of no small theoretical consequence in the context of its interpretation as the law of unattainability of absolute temperature zero. From the positions of equilibrium thermodynamics such a conclusion may be drawn taking into consideration that on approaching the absolute temperature zero all isothermal processes are becoming simultaneously adiabatic. Hence at T=0 heat exchange becomes impossible and this state can not be attained yet by the reversible heat exchange. This becomes even more evident taking into account the irreversibility of heat exchange, i.e. the provision that a temperature differential between a body and the environment is required to provide it. In this case, to attain the absolute temperature zero, bodies need to be available with a temperature below zero, which do not occur in nature. This is what W. Nernst, who did not welcome the notion of entropy, interpreted as the unattainability of absolute temperature zero.

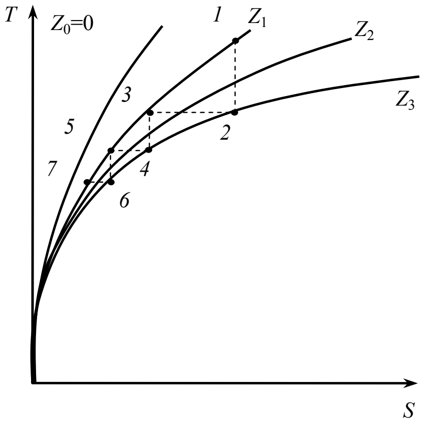

Fig.3.2. To the Law of Unattainability of Absolute Temperature Zero

From here it does not yet follows the impossibility of approaching the absolute temperature zero by whatever other way. It is possible to lower some potential Ψ_i (including temperature T) by varying one of the thermodynamic forces $\mathbf{X}_i$ acting in a system. This, in particular, makes the basis for the method of attaining extremely low temperatures by the adiabatic demagnetization (V. Sychev, 1977). This method is based on the magneto-caloric effect, viz. on the phenomenon of decreasing the temperature T of magnetic material at its magnetization $\mathbf{Z}_{м}$ depressing, the decreasing rate being defined by the derivative $(\partial T/\partial \mathbf{H})_{S,\mathrm{p}}$. At quite low temperatures this derivative reaches a noticeable value for a number of magnetic materials, which allows realizing the method offered by Debye and Gioque in 1926. Fig.4.2 explains the process by a T–S diagram. The diagram depicts a family of magnetization curves $\mathbf{Z}_{м}$ = const. Since with the temperature decreasing, the entropy ceases depending on whatever parameters of magnetic material (including $\mathbf{Z}_{м}$), all curves at $T = 0$ converge to the same point. In this case the character of the curves themselves depends on the behavior of the heat capacity c_p of the magnetic material nearby the absolute temperature zero. Since with the temperature decreasing, the heat capacity c_p of a number of magnetic materials decreases even faster, the curves at T=0 have a common vertical tangent. Let point 1 ($S > 0$) on the T–S diagram characterizes the initial state of the magnetic material. Then running a single adiabatic demagnetization process (1–2) to the state $\mathbf{Z}_{м} = 0$ we are still quite far from the state T=0. However we can isothermally magnetize the material once again simultaneously removing the heat herein released to an intermediate coolant (2-3) and then repeat the adiabatic demagnetization. Iterating the process it is possible to become asymptotic to the absolute temperature zero. Temperatures of 0.001K have been reached by this way at present time. Thus one can only insist on unattainability of absolute temperature zero for a single process. In this context it is advisably to put forward one more, let us say, philosophical sanction. The unattainability of absolute temperature zero or any other generalized potential means the "indestructibility" of heat or any other form of energy at all and by whatever way. It follows from here that all known forms of energy either have always existed or were "created" for ever and aye by a disposition of Providence so that new forms of energy can not occur in nature. Antiscientific character of such a deduction is evident. Therefore, from the positions of thermokinetics it is more preferable to adhere to the "asymptotic attainability" of absolute temperature zero as a result of infinite sequence of adiabatic-isothermal processes (1-2-3-4-5-6-7-etc.). From this viewpoint the heat or any other form of energy can "degenerate" under certain conditions. For the heat form of motion featuring a "symbiosis" of kinetic and potential energies of particles this can occur in two events – at infinitely high compression, when kinetic energy of all kinds of particle motion degenerates, and at infinite expansion (scattering) of particles, when potential energy of their interaction degenerates. Both events apparently occur in the Universe, which makes the extension of the thermodynamic laws to the Universe an impermissible extrapolation.

3.6. Principle of Entropy Maximum as Equilibrium Condition

The equilibrium self-non-disturbance principle is one of the primary postulates of classic thermodynamics. It reads that *an isolated system with time always comes to a state of thermodynamic equilibrium, and only an action from outside can make it out of this state.* Being a result of the experience accrued, this statement is a basis of thermodynamics as a whole and defines the limits of its applicability.

From the viewpoint of statistical physics internal equilibrium in a system corresponds to such a state of the incessantly moving micro-particles of the system which occurs most frequently and thus is most probable. From this it follows that the spontaneous transition of a system to equilibrium is not an absolute law of nature, but expresses just the most probable behavior of the system. Based on this principle, thermodynamics restricts the spectrum of the systems that may be considered as thermodynamic and leaves out of consideration the ones that develop missing equilibrium. Such systems, in particular, include microscopic objects, which never ceasing motion leads to their spontaneous deviation from the most probable state (system fluctuations). Here come also systems of galactic size, where, due to lag of interaction, instead of dying the fluctuations down their "build-up" may arise like in the regulation systems with positive (regenerative) feedback. Such systems become the subjects of thermokinetics allowing for processes of "self-ordering" of a number of degrees of freedom against disordering of other ones and never coming to the total equilibrium state. However, this discipline is also rested on the statistical foundation of the collective behavior of a great number of particles (collective degrees of freedom) resulting in the macroscopic (observable) character which the microscopic motion acquires. From this it follows that the thermodynamic and statistical approaches are not alternative, but mutually complementary.

In accordance with its laws classic thermodynamics deals with transitions in-between two and more equilibrium states disregarding the kinetics of these transitions. Therefore the concept of equilibrium and equilibrium conditions are top-priorities in this theory.

The theory of system equilibrium and stability was first developed by Lagrange for mechanical systems. That was based on the virtual displacement principle. It says that a mechanical system at ideal constraints remains in equilibrium providing the sum of works done by all forces at any virtual (possible) displacement of the system is equal to zero. That theory was then extended by Gibbs to thermodynamic systems. The peculiarity of that principle as applied to thermodynamics was that depending on the conditions of the interface between a system and the environment there were several equilibrium conditions in thermodynamics instead of one condition for mechanical systems. In particular, the condition of stable equilibrium for isolated systems means maximality of their entropy:

$$\delta S = 0,\ \delta^2 S < 0\ , \tag{3.6.1}$$

where δS, $\delta^2 S$ – respectively, first- and second-order variation of entropy. The equality of the first-order variation of entropy δS to zero means equilibrium, while the negativity of its second-order variation $\delta^2 S$ (maximality of entropy) characterizes the stability of equilibrium.

The general method of definition of equilibrium conditions set forth by Gibbs may be instantiated by a system that has, besides the thermal and the mechanical degrees of freedom, also some i^{th} degrees of freedom (related to, e.g., interchange of the k^{th} substances between the parts of the system). Let us consider a heterogeneous in whole system consisting of two homogeneous subsystems (phases or zones). Designating the parameters of these subsystems with correspondingly one or two primes let us express, according to (2.3.6), the variations of energy δS for both subsystems as:

$$\delta U' = T'\delta S' - p'\delta V' + \Psi_i'\,\delta\Theta_i'\,, \tag{3.6.2}$$

$$\delta U'' = T''\delta S'' - p''\delta V'' + \Psi_i''\,\delta\Theta_i''\,. \tag{3.6.3}$$

For the sake of simplicity we have only considered here one additional degree of freedom with the coordinate Θ_i and the potential Ψ_i, which, however, does not affect the generality of consideration. Since the system in whole is isolated, the variations of the extensive coordinates in (3.6.2) and (3.6.3) have the constraints imposed:

$$\delta U' + \delta U'' = 0;\ \delta S' + \delta S'' = 0; \tag{3.6.4}$$

$$\delta V' + \delta V'' = 0;\ \delta\Theta_{\mathrm{i}}' + \delta\Theta_i'' = 0. \tag{3.6.5}$$

To use the principle of entropy maximality in equilibrium conditions, let us represent equations (3.6.2)-(3.6.3), allowing for (3.6.4)-(3.6.5), in the form:

$$\delta S = (1/T' - 1/T'')\delta U' + (p'/T' - p''/T'')\delta V' + (\Psi_i'/T' - \Psi_i''/T'')\delta\Theta_{\mathrm{i}}' = 0. \tag{3.6.6}$$

Since the variations $\delta E'$, δV' and $\delta\Theta_i'$ caused by, respectively, possible heat exchange, increase of volume of one part at the expense of other and by transfer of the i^{th} energy carrier, do not depend on each other and can take any values, the necessary and sufficient criteria of equilibrium assume the form:

$$T' = T''\ \text{(thermal equilibrium)}; \tag{3.6.7}$$

$$p' = p'' \text{ (mechanical equilibrium);} \qquad (3.6.8)$$

$$\Psi_i' = \Psi_i'' \text{ (}i^{\text{th}}\text{ - kind equilibrium).} \qquad (3.6.9)$$

However, the equilibrium conditions above defined do not allow for some zones which may form in each of the subsystems and featuring new properties, e.g., drop formation in supersaturated steam, graining in oversaturated solution, etc. Additional equilibrium conditions excluding such processes are usually called equilibrium stability conditions (R. Haase, 1964). If transition of such a kind is impossible, the equilibrium (or the system) is referred to as stable. If the transition under consideration may occur at only discrete (finite) variations of state, the system is relatively stable (meta-stable). If the said transition occurs at infinitesimal variations of state, the system is absolutely unstable (labile).

The above-mentioned maximum of entropy is a starting point for stating the stability conditions. In this case, however, along with the absence of the first-order variation of entropy the inequality sign appears $đS \le 0$ allowing for unilateral state variations. In many cases, to define the equilibrium and equilibrium stability conditions, characteristic functions (thermodynamic potentials) appear more convenient, such as the internal energy U (at S, V, Θ_i = const), the enthalpy $H = U + pV$ (at S, Θ_i = const), the Helmholtz "free energy" $\Gamma = U - TS$ (at V, Θ_i = const), the Gibbs "free enthalpy" $G = U + pV - TS$ (at T, p, Θ_i = const), etc. Their variations form a system of 8 inequalities of the type described above (R. Haase, 1964). Since each of these functions is the potential for only definite set of independent variables, the choice of the corresponding function is required for a particular set of variables. To provide this, it is necessary to address a number of mnemonic codes facilitating storage of the equilibrium criteria relevant for particular sets of variables. It will be shown hereafter (in chapter 9) that this difficulty may be avoided using the inergy E of a system as a universal thermodynamic potential. Dividing energy into inergy and anergy allows also integrating the first and the second laws of thermodynamics and expressing its fundamental law most concisely, *"When whatever spontaneous processes are running in isolated systems, their inergy goes over into anergy with their sum remaining constant"*.

Consideration of the fundamental laws of equilibrium thermodynamics as deductions of the unified theory of real processes allows presenting these laws in the most evident form. The assumptions laid in the foundation of the real-process theory become more distinct, while the reasons of its narrowness – more cognizable. This enables tracing out ways toward generalization of the classic theory and overcoming the difficulties revealed. These ways will be threaded hereafter in the consecutive chapters of this book.

The same entropy maximum is a starting point for laying down the stability conditions. In this case, however, along with the first variation of entropy being absent the inequality sign $đS \leq 0$ appears, which considers the possibility of unilateral state variations. In many cases, in order to lay down the equilibrium and stability conditions, characteristic functions (thermodynamic potentials) appear to be more appropriate. The definition of such functions is essentially simplified with the basic equation of thermokinetics used in the form of (2.2.5) wherein the expression $\Sigma_i \mathbf{X}_i \cdot d\mathbf{Z}_i$ characterizes the elementary useful work $đW$ the system does. Basing on this and applying the Legendre transformation $\Psi_i d\Theta_i = d\Psi_i\Theta_i - \Theta_i d\Psi_i$ to the terms of its first sum with consideration of (2.5.6) gives:

$$đW = -\, d(U - \Sigma_i\Psi_i\Theta_i) + \Sigma_i\Theta_i d\Psi_i\,. \tag{3.6.10}$$

For the particular case of a thermo-mechanical system with two degrees of freedom ($\Psi_1 \equiv T$; $\Theta_1 \equiv S$; $\Psi_2 = p$; $\Theta_2 = -V$) the function $U - TS + pV$ has been termed as the Gibbs energy G. Then at $p,T =$ const

$$đW = -\,[d\mathrm{G}]_{p,T}\,, \tag{3.6.11}$$

i.e. the work the system does at $p,T =$ const besides the expansion work, is equal to the Gibbs energy loss. Based on this fact, the value G is also called the isobaric-isothermal potential or free enthalpy $G = H - TS$ (where $H \equiv U + pV$ – enthalpy). With $V,T =$ const the isobaric-isothermal potential gives way to the isochoric-isothermal potential $\Gamma \equiv U - TS$ Massieu first introduced (1869) and H. Helmholtz called as free energy:

$$đW = -\,[d\Gamma]_{V,T}\,. \tag{3.6.12}$$

Eventually, with $V, S =$ const the role of potential is played by the system internal energy U:

$$đW = -\,[dU]_{V,S}\,. \tag{3.6.13}$$

Another significant property of thermodynamic potentials is their capability to play the role of characteristic functions. The term “characteristic function” was introduced by Massieu (1869) – the first one who realized the practicability of using those functions $\Gamma(T,V)$ in order to find thermodynamic properties of a system as its derivatives. In particular, the system pressure p can be found as the first derivative of the system internal energy U with respect to the volume V (providing the entropy S being constant), while the temperature T – as the derivative of the system internal energy U with respect to the entropy S (at $V =$ const):

$$p = -(\partial U/\partial V); \; T = (\partial U/\partial S). \tag{3.6.14}$$

Similarly the system entropy S can be found as the first derivative of the free energy F with respect to the temperature T, while the isochoric heat capacity C_v – as its second derivative:

$$S = -(\partial F/\partial T), \; C_v = -T(\partial^2 F/\partial T^2). \tag{3.6.15}$$

A system at equilibrium is incapable for work. This means that the thermodynamic potentials at this state reach their minimal value equal to zero. This allows finding the equilibrium and stability conditions for non-isolated thermodynamic systems proceeding from minimum of thermodynamic potentials as a condition:

$$(\delta^2 H)_S > 0 \; ; (\delta^2 G)_{p,T} > 0; (\delta^2 F)_{V,T} > 0. \tag{3.6.16}$$

Since each of these functions is the potential at only a certain set of independent variables, each particular set of the independent variables requires a particular function to be chosen from their total number. Taking into account that this number reaches eight in the general case of open systems, we are thus led to a number of mnemonic rules to facilitate remembering the equilibrium criterion acceptable for a particular case. This difficulty may be avoided later on (see Chapter 14) through application of the system inergy E as a universal thermodynamic potential.

It is worth noticing in conclusion that the substantiation of the basic laws pertaining to equilibrium thermodynamics as consequences from thermokinetics allows to refuse their postulation and to expose the very gist of them. This makes the assumptions laid into the foundation of this theory clearer and the reasons of its inferiority more understandable. This allows outlining the ways how to generalize the classic theory and to overcome the difficulties revealed. These ways will be realized in subsequent chapters of the book.

Chapter 4

THERMODYNAMICS OF IRREVERSIBLE PROCESSES

The rise of engineering interest in phenomena at the interface between various disciplines and perception of their close relation with the phenomena of the energy dissipation led to creating, in the early 20th century, the thermodynamic theory of real process rate. This field in macroscopic physics of the 20th century was named the theory of irreversible processes (L. Onsager, 1931; I. Prigogine, 1947, 1955; H. Cazimir, 1945; K. Denbigh, 1951; S. De Groot, 1952, 1962; J. Meixner, 1954, I. Gyarmati, 1960, 1970; R. Haase, 1962, etc.). It has enriched the theoretical mind of the 20th century with a number of general physics principles and notably contributed to cognition of the in-depth interrelations between different-type phenomena. That contribution was appreciated by two Nobel prizes awarded in the field (Onsager, 1968; I. Prigogine, 1977).

However, the theory of irreversible processes (TIP) was constructed by extrapolating classic thermodynamics beyond the strict framework of applicability of its system equilibrium and process reversibility concepts. This has led the TIP to its losing the rigor and completeness intrinsic for the classic thermodynamic method. In this context it becomes a question of significant importance to provide a consistent thermodynamic substantiation of the TIP fundamentals from the more general positions of thermodynamics.

4.1. Theory of Dissipation Process Rate in the Making

More than centenary had passed before it became clear that "thermodynamics unaware of time" (to a Brian's figurative locution) was substantially thermostatics wherein only Fourier's, Navier's, Ohm's, Fick's, Darcy's, Newton's, etc. equations prefigured the coming theory of non-static (running with finite rate) processes, viz. thermokinetics. However, the development in that direction demanded introducing in thermodynamics the transfer concepts intrinsically extraneous for it. One of these belongs to N. Umov (1873), who wrote the law of conservation of energy in terms of the mass elements of resilient media as:

$$\partial \rho\varepsilon / \partial t + \nabla \cdot \mathbf{j}_e^{\mathrm{o}} = 0 , \qquad (4.1.1)$$

where ρ, ε – density of a system and its specific energy, respectively; $\mathbf{j}_e^{\mathrm{o}}$ – local density of the energy flow across the stationary borders of the system; t – time.

The flow concept in application to entropy (G. Jaumann, 1911) became another stride. Note, that application was quite novel, because of the statistic-mechanical interpretation of entropy as a measure of state probability for which the transfer concept is absolutely senseless. G. Jaumann set forth the equation of entropy balance:

$$\partial(\rho\Sigma s)/\partial t + \nabla\cdot\mathbf{j}_s^{o} = \sigma_s\,, \tag{4.1.2}$$

where the specific entropy variation rate s (J/kg·K) is represented as a consequence, on the one hand, of its transfer across the system borders by the entropy flow with the density $\mathbf{j}_s$ ($\mathrm{W/m^2 \cdot K}$), while, on the other hand, of availability of its internal sources with the volume density σ_s ($\mathrm{W/m^3 \cdot K}$). A little bit later De Donder (1927) related the entropy source σ_s with the rate of the rth chemical reactions in the volume unit w_r of the system and with the affinity A_r of those reactions:

$$\sigma_s = \Sigma_r\, A_r w_r /T\,. \tag{4.1.3}$$

That was how the concepts of flow and process rate started their introduction into thermodynamics. The most decisive move in that direction was not, however, made, until 1931 (L. Onsager). Onsager built his theory of physicochemical process rate (he named it “quasi-thermodynamics”) based on the expression for the entropy generation rate, having thus emphasized the irreversible part of real phenomena. The entropy S of a closed adiabatic isolated system in equilibrium state is known to be maximal. If the parameters x_1, x_2 ...,x_n (temperature T, pressure p, concentrations c_k of kth substances, etc.) of non-equilibrium state differ from their equilibrium values $x_{1\mathrm{o}}$, $x_{2\mathrm{o}}$,..., x_{no} by a value of $\alpha_i = x_i - x_{i\mathrm{o}}$, it is naturally to assume that the difference between the entropies of the current S and equilibrium S_o states $\Delta S = S - S_0$ is a some function of $\alpha_1, \alpha_2,...,\alpha_\mathrm{n}$. In this case the reason of the ith scalar process generation (the scalar thermodynamic force X_i) and the generalized rate of this process (named by L. Onsager the flow J_i) could be found from the expression for the entropy generation rate:

$$dS/dt = \Sigma_i(\partial S/\partial\alpha_i)\, d\alpha_i/dt = \Sigma_i X_i J_i\,, \tag{4.1.4}$$

where

$$X_i = (\partial S/\partial\alpha_i); \quad J_i = d\alpha_i/dt\,. \tag{4.1.5}$$

Thus L. Onsager endued the force X_i with a meaning quite different from that in Newton’s mechanics and construed it as a parameter measuring the deviation of a system from internal equilibrium. At the same time L. Onsager postulated that for minor deviation from thermodynamic equilibrium any of the flows J_i obeyed the law of linear dependence on all the thermodynamic forces X_j active in the system:

$$J_i = \Sigma_j L_{ij} X_j . \quad (i,j = 1, 2, \ldots, n) . \tag{4.1.6}$$

L. Onsager referred to those laws of relaxation processes, as well as the associated coefficients L_{ij}, as "phenomenological" (i.e. practice-based). The off-diagonal summands in expression (4.1.6) were introduced by Onsager to allow for various "superposition" (interrelation) effects of different-type irreversible processes running simultaneously in the same spatial zones.

The proof of reciprocity relationships between the "off-diagonal" phenomenological coefficients L_{ij} and L_{ji} ($i \neq j$) was most important in the L. Onsager's theory:

$$L_{ij} = L_{ji} . \tag{4.1.7}$$

These symmetry conditions are called the reciprocity relationships. They reduce the number of the coefficients L_{ij} to be experimentally defined from n (for mere empirical description) down to $n(n+1)/2$ (where n – a number of independent flows) and lead to setting up a before unknown relationship between the rates of different-type irreversible processes. L. Onsager was afterward awarded the Nobel Prize (1968) for his studies in that field. Those studies attributed to non-equilibrium thermodynamics just as much as the R. Clausius' studies to the making of classic thermodynamics. They have embodied the odds and ends of concepts and facts representing them in an accessible and understandable form. Their publication made a good start to the intensive development of the TIP in macroscopic and statistical physics. After Onsager, H. Cazimir (1945) extended the Onsager's theory to cover vector processes, having herein proved that in case the α– and β–type forces (even and odd time functions) acted simultaneously, the reciprocity relationships (6) would go over into the anti–symmetry conditions:

$$L_{ij} = -L_{ji} \tag{4.1.8}$$

A little bit later (1956-62) I. Prigogine (the 1977 Nobel prizewinner) based on Curie's symmetry law showed that in case the scalar and vector processes ran simultaneously, only the processes of the same (or even) tensor range could interact (superimpose). Insufficiency of the Onsager's postulate (see 4.1.6) was thus revealed. Besides, I. Prigogine showed that the stationary (unvaried with time) state of non–equilibrium systems was characterized by minimal rate of the entropy generation (minimal entropy production dS/dt) and corresponded to disappearance of the flows J_j

subscript–similar to the non–fixed forces X_j. He also showed that the part of the entropy production d_XS/dt associated with the force variation decreased as having approached the stationary state. That allowed further solving a number of problems associated with the evolution of non-equilibrium systems.

An especially rapid development of the TIP started post–World War II. The interest in that field of knowledge was caused not only by its general theoretical significance, but rather its important applications having been outlined in the forties and fifties and having involved the thermal diffusion isotope separation, the allowance for additional terms in the hydrodynamic equations for missile art and plasma physics, the development of membrane technique, biophysics, etc. Due to the resumptive studies of H. Cazimir (1945), I. Prigogine (1947, 1976), K. Denbigh (1951), S. De Groot (1952, 1962), J. Meixner (1954), I. Gyarmati (1960, 1970), R. Haase (1962), etc. this theory has become a separate field of thermodynamics with its own method and the certain spectrum of the problems to be solved.

Important investigations in this field have been carried out by domestic scientists. In particular, in 1947 M. Leontovich and L. Mandelshtamm developed a thermodynamic theory of acoustic relaxation distinguished from the Onsager's theory. L Landau and E. Livshits greatly contributed to the TIP, when showed in 1951 that under the symmetry conditions (4.1.7) the phenomenological coefficients in Onsager equation were terms of a substantially positive matrix and therefore had the constraint imposed:

$$(L_{ij} + L_{ji})^2 < 4L_{ii}L_{jj} . \tag{4.1.9}$$

Domestic scientists were among those, who much advanced practical applications of that theory to various processes, viz. chemical (Bakhareva, 1967; Bulatov and Lundin, 1984), metallurgical (Veinik, 1966; Gurov, 1978), biological (Rubin, 1984; Gladyshev, 1988, etc.), as well as a popularization of that field of knowledge (Zhukovsky, 1979; Burdakov, 1985, etc.). They especially contributed to having developed statistical methods of substantiation and construction of the linear and non-linear irreversible process theory (Zubarev, 1971; Stratonovich, 1985, Kvasnikov, 1987; Bazarov, 1989, etc.).

The development of the phenomenological and statistical TIP has advanced the approximation of the heat-mass transfer theory to hydrodynamics, electrodynamics and continuum mechanics. It appeared to have been especially useful to study phenomena at interfaces between those disciplines. However, those theories never did eliminate the abovementioned line of demarcation between thermodynamics and the heat transfer theory. The reason is that the TIP is restricted to studying the dissipation processes like heat conductivity, electric conductivity, diffusion, as well as effects of their superposition, but does not deal with the processes of useful energy conversion, which are the main object of investigation in thermodynamics. This is the reason why the necessity appeared to call thermodynamics into being as a unified theory of energy transfer and conversion rate and capacity, which, unlike W. Thomson's "pseudo-thermostatics" and L. Onsager's "quasi-thermodynamics", would not "unfile" some part of a phenomenon, but would cover the entire spectrum of real processes.

4.2. Motive Forces and Generalized Rates of Transfer Processes

As it follows from expression (4.1.4), the selection of the motive forces X_i and the flows J_i in the TIP depends on how the expression for the entropy generation rate is broken up into separate components. The only demand herein is that the flows to be linearly independent and, at equilibrium, become zero along with the thermodynamic forces. Such arbitrariness was acceptable till the moment the different-type summands $X_i{\cdot}J_i$ characterized the power of the same energy dissipation processes. However, that arbitrary rule appeared to have been absolutely unacceptable in terms of the useful energy conversion processes, e.g. in biophysics, since that would lead to an equivocal assessment of the energy converter efficiency (see chapters 16, 17). Furthermore, expression (4.1.4) is inapplicable to evaluate the reversible component of the motive forces, since the reversible processes are known to have no influence on entropy (M.P. Vukalovich, I.I. Novikov, 1968; I.P. Bazarov, 1991). If, e.g., chemical reactions are described running in an ideal fuel cell (without entropy production due to thermodynamic irreversibility of chemical reactions), expression (4.1.4) gives zero value for these forces. For this reason it does not allow finding the true value of the motive forces including a reversible component. Moreover, in some instances expression (4.1.4) does not allow defining even the sign of these forces. If useful work is done on a system, the product of the subscript-similar forces $\mathbf{X}_i$ and flows $\mathbf{J}_i$ appears to be always negative, whereas the value dS/dt in (4.1.4) being always positive. Furthermore, all summands of phenomenological laws (4.1.5) are always positive, whereas for useful energy conversion processes they are partly negative (the flow $\mathbf{J}_i$ decreases as the forces $\mathbf{X}_j$ being overcome increase). Besides, from relationship (4.1.7) some relative efficiency constraints ensue, which are alien for real energy converters. As a result of the said, the vastest spectrum of real processes with a relative efficiency above zero appeared to have been "extra vires" the TIP.

Thermodynamics allows avoiding this arbitrariness, when referring the forces $\mathbf{X}_j$ and flows $\mathbf{J}_i$ to the non-equilibrium state parameters, and enables finding them irrespectively of what causes them – either the dissipation or useful work done. As shown in chapter 2, any vector processes arise providing there is no internal equilibrium in a system, i.e. they are heterogeneous (M.P. Vukalovich, I.I. Novikov, 1968). This allows finding the thermodynamic forces of any nature $\mathbf{X}_i$ as the derivatives of the system energy E with respect to the corresponding distribution moment

$$\mathbf{X}_i \equiv -(\partial E/\partial \mathbf{Z}_i), \tag{4.2.1}$$

while the flows $\mathbf{J}_i$ – as the partial time derivatives with respect to these moments:

$$\mathbf{J}_i = \partial \mathbf{Z}_i/\partial t = \Theta_i \mathbf{v}_i\,. \tag{4.2.2}$$

Such a definition of thermodynamic forces univocally represents their local values $\mathbf{x}_i$ in terms of negative gradients of the generalized potentials $\mathbf{x}_i \equiv -\nabla\psi_i$. This approach endues the thermodynamic forces with a concrete physical meaning as intensive measure of system heterogeneity. Their "global" (for a system in whole) analogs $\mathbf{X}_i$ are herein the system-averaged values of these gradients. As shown in chapter 2, the forces $\mathbf{X}_i$ mean the forces $\mathbf{F}_i$ in their traditional (Newtonian) interpretation per a unit amount of the energy carrier $\mathbf{X}_i = \mathbf{F}_i/\Theta_i$, i.e. are analogs of the specific mass, volume, surface, etc. forces in hydrodynamics. Unlike them, the thermodynamic forces in the TIP may be represented as $\nabla\psi_i$, $T^{1}\nabla\psi_i$, $\nabla(1/\psi_i)$, $\theta_i\nabla\psi/T$, etc. (De Groot, 1956). This, naturally, deprives them of an explicit physical meaning and impedes comprehension of the backbone of the phenomena occurring.

The said appertains as well to flows that may have different dimensionalities and meanings depending on the way the product $\mathbf{X}_i \cdot \mathbf{J}_i$ is broken up into cofactors. Besides, flows in the TIP are often construed (after L. Onsager) as the generalized rates of scalar processes $w_i = d\Theta_i/dt$, e.g. of chemical reactions. Thermodynamics "restitutes" the general physical conception of flow as a vector value thus allowing to distinguish it from the generalized rate w_i of scalar process not only physically, but also analytically.

4.3. Entropy Balance Equation and Dissipation Rate

The core of the TIP comprises the balance equations for mass, momentum, charge, angular momentum and energy of multi-component systems, which allow further determining the entropy balance and finding from this the motive forces and generalized rates for a system under consideration. Setting up these balance equations is the most burdensome and laborious part of the TIP and its applications, especially taking into account that each of the equations mentioned has a local (spatial)

$$\partial\rho_i/\partial t + \nabla\cdot\mathbf{j}_i^{\,o} = \sigma_i \qquad (4.3.1)$$

and a substantial (material) form :

$$\rho d\theta_i/dt + \nabla\cdot\mathbf{j}_i = \sigma_i\,, \qquad (4.3.2)$$

where $\mathbf{j}_i^{\,o} = \rho\theta_i\mathbf{v}_i$, $\mathbf{j}_i = \rho\theta_i(\mathbf{v}_i - \mathbf{v}_o)$ – density, respectively, of local and substantial flow of the field value Θ_i; $\mathbf{v}_i$, $\mathbf{v}_o$ – transfer velocity, respectively, of the Θ_i value and selected volume element in the stationary (laboratory) coordinate system; σ_i – density of internal source for the value Θ_i.

To set up such balance equations for a particular field value Θ_i, thorough knowledge of an applicable scientific discipline is necessary, which should precede the associated TIP application. Naturally, one can hardly expect some corrections to such disciplines would be done.

Next step toward a TIP application denotes setting up energy balance equations – for both kinetic (translation and rotation) and potential (mechanical, electromagnetic, chemical, etc.) energies in some form or other (spatial or material). These equations are similar to expressions (4.3.1) and (4.3.2) except that θ_i , $\mathbf{j}_i^{\,o}$,$\mathbf{j}_i$ and σ_i are construed as specific values of a relevant energy form, densities of their flows and internal sources (if applicable). Since classic thermodynamics does not operate in terms of time as a physical parameter, the above data is also entirely taken from outside, viz. from applicable scientific disciplines. Only then thermodynamics proper starts off with using the joint equation of the first and second laws of classic thermodynamics for open systems in the form of the Gibbs relationship (see 2.5.1). Using it for irreversible processes under investigation is based on the local equilibrium hypothesis which assumes this equation to be true locally (for continuum elements) despite the gradients of various potentials presenting in the elements and the irreversible processes running in them (internal sources of the entropy σ_s presenting there). From joint consideration of equation (2.5.1) and the abovementioned balance equations for mass, momentum, charge and angular momentum the energy balance equation is formulated, which, due to the above, now includes time and an irreversible part can be derived from it. This part formally looks like equation (2.5.1) that contains the sources of all actual values. This is the entropy balance equation that is formulated based on it relating the density of the entropy internal sources σ_s with the generalized rates of scalar and vector processes w_i and $\mathbf{j}_i$ and their motive forces A_r and $\mathbf{x}_i$. Along with the entropy increase rate in a system the dissipation function $T\sigma_s$

$$T\sigma_s = \Sigma_i\, \mathbf{j}_i \cdot \mathbf{x}_i + \Sigma_r A_r w_r\,, \qquad (4.3.3)$$

is often used, defining the energy dissipation rate in the system.

Next step denotes the formulation of Onsager's (4.1.6) kinetic equations (phenomenological laws) for particular processes under investigation. These equations are then considered jointly with Onsager's symmetry conditions (4.1.7) or (4.1.8) in order to define the relationship between the flows $\mathbf{j}_i$ and $\mathbf{j}_j$ arising from the static character of irreversible processes. The last investigation stage reveals the expressions for the so-called "stationary superposition effects" associated with disappearance of one of the actual flows $\mathbf{j}_i$ while the system non-equilibrium state maintained.

As it follows from the above, the superposition effect definition based on the TIP is a quite complicated multi-stage problem involving the whole intellectual arsenal of special disciplines. This makes thermokinetics even more attractive as a short cut method of finding a solution to the problem. This becomes possible due to the fact that the thermodynamic equations of (2.3.1) type already contain time, flows and thermodynamic forces and, therefore, do not need setting up complicated mass, charge, momentum, energy and entropy balance equations. These equations eliminate whatever arbitrariness in choosing the physical values defining motive forces and generalized rates of scalar and vector processes. Their meaning and analytical expression are unequivocally determined by choosing the coordinate Θ_i as a quantitative measure of a particular energy form carrier. In this case the thermodynamic forces, according to (2.2.8), are expressed in terms of negative gradients of the generalized potential Θ_i-related, while the flows $\mathbf{J}_i$ or $\mathbf{j}_i$ – by the product of these values and the rate of their transfer under the action of the forces $\mathbf{X}_i$ or $\mathbf{x}_i$. Applications of this method to various problems will be specifically instantiated in the chapters following hereafter. Other advantages of this approach will simultaneously become evident.

4.4. Phenomenological Laws of Transfer Processes

The Onsager's assumption that the around-equilibrium generalized rate of a relaxation process (he named this rate the flow J_i) is a linear function of all thermodynamic forces X_j acting in the system (L. Onsager, 1931) is one of the postulates lying in the TIP foundation. This statement named the linearity law is reflected in Onsager's phenomenological laws (see 4.1.6).

Such a (matrix) form of kinetic equations differed from Fourier's, Ohm's, Fick's, Darcy's, Newton's, etc. laws by the presence of additional (off-diagonal) terms (with subscripts $j \neq i$). L. Onsager introduced those terms to allow for the interrelation between different-type phenomena, which he had found experimentally and explained by the "superposition" of different-type flows. He expressed that interrelation in his well-known "reciprocity relationships" which stated the symmetry of the phenomenological coefficients matrix (see 4.1.7).

L. Onsager obtained those relationships based on a known statement of statistical mechanics regarding the reversibility of micro-processes in time under the assumption that the coefficients L_{ij} and L_{ji} were constant, while the subscript-dissimilar flows J_i and J_j were linearly independent and became zero with disappearance of the forces X_i and X_j.

The above postulate was not objected to for more than a half a century and was reproducible in all study guides on irreversible process thermodynamics but with a proviso that according to Curie's symmetry law only processes of the same (or even) tensor order could be interrelated. The question did not anyhow arise in that context how the flows J_i and J_j found to (4.1.4) as the time derivatives of the system independent state parameters $d\alpha_i/dt$ could be interrelated. There were no objections either to the fact that some (moreover the simplest) equations appeared to have been laid as a foundation of the thermodynamic theory which was known to have imported particular data on system properties (expressed in terms of state and transfer equations) "from outside" as uniqueness conditions of a kind while its body of mathematics itself was universal as based on the properties of exact differential of a number of functions of state. The investigators were not at all embarrassed either by the fact that the above postulate undermined the centuries-old buttress of mechanics which stated that each independent process (movement, acceleration, tending to mechanical equilibrium, etc.) was associated with the only (resultant) force and ceased as soon as the force disappeared. Meanwhile, the existence of such a force followed from those equations of anisotropic heat conductivity and electric conductivity which, to Onsager's confession, prefigured his phenomenological laws (1). In fact, for anisotropic heat conductivity and electric conductivity the motive forces $\mathbf{X}_j$ were components of the only force – the negative temperature gradient vector ∇T and the electric field intensity $\mathbf{E}$ ($j = 1,2,3$), respectively. There were also other reasons to doubt the Onsager's postulate was adequate to the point. L. Onsager and his followers, based on equations (4.1.6), derived numerous thermo-mechanical, thermo-electrical, thermo-diffusive, etc. effects from the interrelations between the generalized rates of irreversible processes ran in the same spatial zones, i.e. from the "superposition of flows" or their "mutual entrainment" (N. Bulatov, A. Lundin, 1984). Meanwhile, the above effects are known to reach maximum in the so-called stationary states, when the flows not fixed by an external constraint disappear and, therefore, evidently can not superimpose on those remained. E.g., in electrolytic solutions, where electric conductivity and diffusion phenomena take place, the electric potential difference (Kwinke effect) is maximal whenever current ceases (R. Haase, 1967). This is the case with the Soret effect – arising gradient of the k^{th} substance concentration in a system initially homogeneous with the temperature gradient building up, the concentration gradient reaching maximum as soon as diffusion flows disappear. Hence the reason of such superposition effects should have been searched from the very first not in the interaction between independent flows, but in the superposition of unlike forces as it takes place in mechanics and electrodynamics. Furthermore, the laws (see 4.1.6) L. Onsager named "phenomenological" (i.e. practice-based) are really not so. First of all, the coefficients L_{ij} in Fourier's, Ohm's, Fick's, etc. laws depend on the state parameters of a system (its temperature, pressure, composition, etc.), i.e. are inconstant, whereas the requirement the coefficients L_{ij} to be constant is a substantial part of Onsager's linearity law and bears a principal character. In fact, the forces X_i in the Onsager's theory are functions of the system parameters (temperature T, pressure p, concentration c_k, etc.), therefore the dependence of the coefficients L_{ij} on them would mean their dependence on also the forces X_j, i.e. non-linearity of the phenomenological laws (4.1.6).

Furthermore, according to practice many phenomena arise only when the force reaches some "threshold" value $\boldsymbol{F}_{jo}$ depending on the activation energy for a process under consideration (see chapter 2). However, this circumstance can not be allowed for in Onsager's laws since in this case the flows J_i would disappear earlier than the forces X_i become zero. Lastly, the terms of equation (4.1.6) not necessarily always have the same sign – in many cases the process rate (flow J_i) decreases with increase of the force X_j "being overcome" in this process. So are, as it will be hereafter shown, the phenomenological laws of all processes involving useful energy conversion.

All the said means that Onsager's kinetic laws are not phenomenological, while his postulate itself does not hold water. This nothing but enhances interest toward finding their allowable form proceeding from the demands thermodynamics imposes on the uniqueness conditions of transfer processes. It is easy to show then that the so-called Onsager's phenomenological laws are just a particular case of thermodynamic kinetic equations (2.7.10), when the coefficients K_{ij}^{cp} do not depend on the variables $\Theta_j,\mathbf{F}_j$. As a matter of fact, introducing the thermodynamic force $\mathbf{X}_i \equiv \mathbf{F}_i/\Theta_i$ instead of $\mathbf{F}_j$ and assuming $\mathbf{F}_{jo} = 0$ gives:

$$\mathbf{J}_i = \Sigma_j L_{ij}\,\mathbf{X}_i,\ (i,j = 1, 2, ..., n_j) \qquad (4.4.1)$$

where $L_{ij} = \Theta_j K_{ij}$ – constant coefficients L. Onsager named "phenomenological"; $\mathbf{j}_i$ – density of the flow $\mathbf{J}_i$; $\mathbf{x}_j$ – specific (per unit of the

Θ_j value being transferred) thermodynamic forces $\mathbf{X}_i$ in their " energy" representation (in terms of generalized potential).

The same laws may be expressed as functions of the flows $\mathbf{J}_j$ и $\mathbf{j}_j$:

$$\mathbf{X}_i = \Sigma_j R_{ij}\mathbf{J}_j \quad \text{or} \quad \mathbf{x}_i = \Sigma_j R_{ij}\mathbf{j}_j , \qquad (4.4.2)$$

where R_{ij} – resistance coefficients inverse to the conductivity coefficients L_{ij}.

As one can see, they actually integrate the thermal Θ_j and the kinetic K_{ij} factors. This is the reason why the coefficients L_{ij} or R_{ij} can be referred to neither state parameters nor mere kinetic coefficients (R. Haase, 1967, S.R. De Groot, R. Mazur, 1964, etc.). The values of these coefficients for a particular system are determined experimentally or, as the simplest case, based on statistical theories.

Representation of the phenomenological laws in the form of (4.4.2) allows generalizing the concept of inertia to non-mechanical processes. If to write Newton's law $\mathbf{F} = M\mathbf{a} = d\mathbf{P}/dt$ in the same form of (4.4.2) substituting $\mathbf{F}/M$ for $\mathbf{x}_m$ and the acceleration $\mathbf{a} = d\mathbf{v}/dt$ for $\mathbf{j}_m$ (i.e. to represent the acceleration of a body as the generalized rate of its momentum variation process), then Newton's second law will appear to be a particular case of phenomenological laws (4.4.2), where the off-diagonal coefficient $R_{ji} = M$. In this case the mass M as a measure of inertia of a system takes a meaning of *one of the coefficients of resistance the system offers to running a relevant process (in this case the acceleration process).* Thus the concept of *inertia* as a measure of resistance a system offers to a process running in it acquires the general physics meaning.

4.5. Reciprocal Relation in Transfer Processes

As it has already been mentioned above, the substantiation of reciprocity relationships (4.1.7) was one of the most important statements of the Onsager's theory of irreversible processes (TIP). To substantiate them, he had to apply to the fluctuation theory, microscopic reversibility principle and additional postulate on linearity of the fluctuation damping laws. These three statements outstep the framework of thermodynamics. Therefore in the phenomenological TIP reciprocity relationships (4.1.7) are usually adopted as an additional primary postulate sometimes named (after D. Miller) the "forth law of thermodynamics".

At present statements often and often occur that these relationships do not need any thermodynamic proof since they are statistically substantiated. Discussions about the L. Boltzman's and J. Gibbs' statistical theories, "which grounds are obscure in many ways" (R. Cubo, 1970), are seemingly sunk into oblivion. So, one of the basic statements of statistical mechanics regarding the system ergodicity [1] has remained a hypothesis so far. By the early nineties of the 20th century as a result of the critical analysis conducted on the body of mathematics of statistical mechanics, as well as a result of digital experiments on high-performance computers, it became clear that only hypothetical systems of non-interacting particles might be ergodic. Interaction between particles (e.g. Coulomb or Van der Waals forces) leads to losing ergodicity, therefore the real systems of interacting particles should be described not by statistical, but dynamic methods.

The fact that these reciprocity relationships often vindicate their validity far beyond the restrictions imposed by the method itself of their substantiation evidences the means of proving the relationships L. Onsager offered are inadequate to the point. In fact, the microscopic reversibility principle with one of its statement about equal rates of any direct and reverse molecular processes is valid, strictly speaking, for only equilibrium states. This principle is indubitably inapplicable to the processes of transfer from one non-equilibrium state to other because a system returns to equilibrium state just because the frequency and amplitude of the micro-processes running toward equilibrium dominate. Therefore the reciprocity relationships, providing these really vindicate the principle above, should have been valid in close proximity to the equilibrium state and violated more and more as the system was withdrawing from it. Meanwhile, as it will be instantiated for the helium and argon interrelated filtration and diffusion processes in graphite membranes, to vindicate the reciprocity relationships, just a partial equilibrium is enough, when just a part of the processes running in a system ceases.

Another weak point has been an assumption that the microscopic laws of fluctuation damping obey the same linear phenomenological laws (4.1.6) as the macroscopic processes of heat, substance, charge, etc. transfer. Meanwhile, the real laws of fluctuation damping demonstrate rather exponential character. Even kinetic equations (5.1.6) are, strictly speaking, non-linear. This is especially evident for Fourier's, Ohm's, Fick's, Darcy's, Newton's, etc. laws written in the integral form (in terms of the temperature T, pressure p, concentration c_k, etc. differentials), when the proportionality factors appear to be dependent on the temperature, pressure, concentration, etc. fields.

Lastly, should the linear laws be really necessary to prove the reciprocity relationships, the latter would be violated each time whenever the phenomenological laws cease to be linear. However, as it will be shown hereafter, the reciprocity relationships may be valid as well for the systems,

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[1] The system is referred to as ergodic, where space averaging of a physical value gives the same result as time averaging.

where only the off-diagonal terms of equations (4.1.6) describing the superposition effects are linear. As a result, both the Onsager's theory and TIP in whole fail to reach those rigor and completeness which are intrinsic for the classic thermodynamic method. Therefore C. Truesdall (1975) was positively right, when confirmed that *"once the reciprocity relationships are valid, then the possibility of their merely phenomenological deduction should as well exist"*. Let us show that the Onsager's symmetry conditions ensue directly from the differential relationships of thermodynamics. It follows from independence of the second derivative of the system energy U with respect to the coordinates $\mathbf{Z}_i$ and $\mathbf{Z}_j$:

$$(\partial \mathbf{Z}_i/\partial \mathbf{X}_j) = (\partial \mathbf{Z}_j/\partial \mathbf{X}_i). \tag{4.5.1}$$

These equalities remain valid as well after deriving the total derivatives of both parts with respect to the time t:

$$d(\partial \mathbf{Z}_i/\partial \mathbf{X}_j)/dt = d(\partial \mathbf{Z}_j/\partial \mathbf{X}_i)/dt\,. \tag{4.5.2}$$

In the stationary redistribution processes (at Θ_j, $\boldsymbol{X}_i$ = const) the time differentiation involves only the coordinates $\mathbf{Z}_i$, $\mathbf{Z}_j$. Their time derivatives in the absence of the transfer (recharging) and reorientation processes (Θ_i, $\boldsymbol{\varphi}_i$ = const) define the flows $\mathbf{J}_i$ and $\mathbf{J}_j$. Allowing for this and changing in (4.5.2) the sequence of differentiation with respect to the time t and forces $\mathbf{X}_j$, $\mathbf{X}_i$, gives:

$$(\partial \mathbf{J}_i/\partial \mathbf{X}_j) = (\partial \mathbf{J}_j/\partial \mathbf{X}_i). \tag{4.5.3}$$

These equations may be well referred to the differential reciprocity relationships between flows and forces (V. Etkin, 1991, 1999). They state the cross-impact balance among different-type flows and their motive forces and therefore may be rather named the *reciprocity* relationships than the symmetry conditions of phenomenological coefficients matrix (4.1.7). Risselberghe (1962) was the first who postulated the existence of such-type relationships and proposed to name them the "generalized reciprocity relationships". This is justified since the above Onsager's symmetry conditions may be obtained as a corollary of these relationships for a particular case of linear systems. In fact, applying (4.5.3) to equations (4.1.6) one can obtain:

$$(\partial \mathbf{J}_i/\partial \mathbf{X}_j) = L_{ij} = (\partial \mathbf{J}_j/\partial \mathbf{X}_i) = L_{ji}\,. \tag{4.5.4}$$

Thus the Onsager's reciprocal relations (symmetry conditions) ensue as a corollary of more general differential relationships of thermodynamics and do not need involving whatever statistic-mechanical considerations. Though attempts to substantiate these relationships were made time and again (Gyarmati, 1958, 1960; Li, 1058, 1988; Pitzer, 1961; Risselberghe, 1962), they failed till the lacking coordinates of redistribution processes were introduced. Note, relationships (4.5.3) do not impose any constraints on the process irreversibility degree and the system remoteness from equilibrium. They do not depend either on particular form of the state or transfer equations and, as it will be shown hereafter, are equally applicable to reversible and irreversible processes.

It is worth particular mentioning that from the positions of thermodynamics Onsager's symmetry conditions (4.1.7) are valid as well in the case, when only additional (off-diagonal) terms of equations (4.1.6) are linear, i.e. only the "cross" coefficients L_{ij} or L_{ji} $(i \neq j)$ are constant. This significantly extends the applicability of the differential reciprocity relationships once the diagonal terms of the matrix comprising the phenomenological coefficients L_{ii} or L_{jj} may remain herein any functions of the thermodynamic forces $\mathbf{X}_i$ or $\mathbf{X}_j$ subscript-similar to them. This is what Fourier's, Fick's, Ohm's, Darcy's and Newton's laws are. As for the additional (off-diagonal) terms, these describe less order infinitesimals and in a number of cases may be considered as linear. Thus approaching the problem from the positions of thermodynamics reveals excessiveness of the demand the coefficients L_{ii} or L_{jj} in equations (4.1.6) be constant, which is substantial in all preceding theories of irreversible processes. The demand of close proximity of the system to equilibrium Onsager has laid down in his theory appears to be the same excessive. In fact, the symmetry conditions (see 4.1.7) ensuing from the differential reciprocity relationships (see 4.5.3) are valid for arbitrary large values of the forces $\mathbf{X}_i$ or $\mathbf{X}_j$ in the diagonal terms of the phenomenological laws. This is what explains why the Onsager's theory appears to be applicable far beyond the restrictions imposed by the method itself of their substantiation.

Finally, according to (4.5.4) symmetry conditions (4.1.7) may give place to the anti-symmetry conditions $L_{ij} = -L_{ji}$ (named the Cazimir's relationships in the TIP) providing the terms in equation (4.1.6) have opposite signs. This occurs, when in a transfer process the flow $\mathbf{J}_i$ or $\mathbf{J}_j$ is directed against the forces $\mathbf{X}_j$ or $\mathbf{X}_i$, i.e. "overcomes" them. Such are, in particular, all energy conversion processes, where energy source works against loads. This manifests itself in the occurrence of the so-called "no-load conditions", when with increase of the force $\mathbf{X}_j$ or $\mathbf{X}_i$ being overcome the flow $\mathbf{J}_i$ or $\mathbf{J}_j$ becomes zero. A demonstrative example to the case is loss of the secondary current in the welding transformer with arc extinction. The above statement as well outsteps the TIP, where laws (4.1.6) were postulated by Onsager with only the same sign for all terms.

Thus the reciprocity relationships do not need assumptions on close proximity of a system to equilibrium, constancy of all phenomenological coefficients and linearity of the fluctuation damping laws, which are laid in the foundation of their statistic-mechanical substantiation. According to the above, they ensue from the first laws of thermodynamics and, therefore, feature universal character. This enhances the heuristic value of these relationships and makes them a reliable tool to analyze the interrelations between different-type processes in the real world.

4.6. Law of Minimum Entropy Production

The insufficiency of formalism intrinsic for the linear TIP has caused numerous attempts to give other – variational statement of non-equilibrium thermodynamics. Calculus of variations is a quite universal mathematical method that allows, subject to a suitable model selection, detailing a process under investigation and deriving the associated math laws (including the transfer equations) based on the only variational principle. However, these principles themselves need their substantiation, while their corollaries each time have to be experimentally checked.

L. Onsager set forth the first variational principle of non-equilibrium thermodynamics (1931). He took note of the fact that for the dissipation processes ($J_j = J_j^p$) his phenomenological laws

$$X_i = \Sigma_j R_{ij} J_j^{\mathrm{p}} \,.\, (i, j = 1, 2, \ldots, n) \,, \tag{4.6.1}$$

(where $\mathrm{R}_{ij} = \mathrm{L}_{ij}^{-1}$ – resistance coefficients inverse to the phenomenological conductivity coefficients L_{ij}) along with the reciprocity relationships

$$R_{ij} = R_{ji} \tag{4.6.2 }$$

are equivalent to the statement that the expression $\Sigma_j X_{\mathrm{i}} dJ_j^p$ is the exact differential of some potential function $\Phi(J_i^p, J_j^p) = ½\, \Sigma_{\mathrm{j}}\, \mathrm{R}_{\mathrm{ij}}\, J_i^p J_j^p$, the first derivatives of which with respect to the flows J_j^p give linear phenomenological laws (4.6.1), while the mixed derivatives $(\partial^2\Phi/\partial J_i^p \partial J_j^p)$ give reciprocity relationships (4.6.2). The function $\Pi_X(\mathrm{X_i}, \mathrm{X_j}) = ½\, \Sigma_{\mathrm{j}}\, L_{ij} X_i X_j$ features the same properties, which leads to phenomenological laws (4.1.6) and reciprocity relationships (4.1.7). In linear systems the functions $\Phi(J_i, J_j)$ and $\Pi_X(X_i, X_j)$ are equal to half the dissipation function $P = T\sigma_{\mathrm{s}}$

$$\Phi_J(J_i^{\mathrm{p}}, J_j^{\mathrm{p}}) = \Pi_X(X_i, X_j) = ½\, P \tag{4.6.3}$$

and are named the local dissipation potentials (expressed in terms of flows and forces, respectively).

It is easy to make sure that the variation of the potentials $\Phi_J(J_i^{\mathrm{p}}, J_j^{\mathrm{p}})$ and $\Pi_X(X_i, X_j)$ with respect to flows at all forces X_j being constant gives the same value of X_j so that the extreme condition is met:

$$\delta[Y(X_j, J_j^{\mathrm{p}}) - \Phi_J(J_i^{\mathrm{p}}, J_j^{\mathrm{p}})]_{Xj} = 0, \qquad (4.6.4)$$

where δ – variation symbol; the subscript to the function being varied denotes the value remaining constant at variation.

The extreme determined by (4.6.4) can be only the maximum owing to positive determinacy of the dissipation potentials. Therefore L. Onsager named statement (4.6.4) the “principle of least energy dissipation”.

Another form of the same principle was later offered by I. Gyarmati (1974) for the functional $Y(X_j, J_j^p)$ - $\Pi_X(X_i, X_j)$ expressed in terms of forces at constant flows:

$$\delta(Y - \Pi_X) = \Sigma_j (J_j^{\mathrm{p}} - \partial\Pi/\partial X_j)\delta X_j = 0. \qquad (4.6.5)$$

I.Gyarmati further merged both forms of that principle in a single variational condition:

$$\delta(Y - \Phi_J - \Pi_X) = 0, \qquad (4.6.6)$$

where variation may be conducted with respect to both forces and flows. This condition reflects the extremity of the so-called “Onsager-Machlup’s function” (the expression in brackets) and includes all statements of Onsager’s “quasi-thermodyanmics”.

A number of other variational principles convenient for particular applications were offered by G. Tzigler (1966). As I. Bakhareva then showed (1967), all the said variational principles could be obtained by simple transformations of the same expression:

$$\Sigma_j(\partial\Phi_J / \partial J_j^{\mathrm{p}} - X_j)\delta\alpha_i = 0. \qquad (4.6.7)$$

This eliminates the necessity to provide thermodynamic substantiation for each of the principles mentioned – it is enough to substantiate the validity of condition (4.6.7). This may be done based on some (linear or non-linear) phenomenological laws. In fact, whereas differential reciprocity relationships (4.5.3) do not depend on character of these laws, the differential form

$$\Sigma_j J_j^{\mathrm{p}} dX_j = d\Pi_X \qquad (4.6.8)$$

is always the exact differential of the dissipation function Π. Applying the Legendre transformation, it can be easily shown that the expression $\Sigma_j X_j dJ_j^p$

is as well the exact differential of other function of state of the non-equilibrium system Φ. From this it follows that $\partial\Phi/\partial J_j^p = X_j$. Expression (4.6.7) is thereby valid with the same generality degree, i.e. not only for linear systems, but also in a more general case, when the differential reciprocity relationships are valid. In this case $P = \Phi_J + \Pi$ even when $\Phi_J \neq \Pi_X$.

The law of *minimum entropy production* occupies a special place among the TIP extreme principles. Its first statement belongs to I. Prigogine (1947) and refers to discontinuous systems. According to the Prigogine-proven theorem the minimal production of entropy $\sigma_s = \min$ in a stationary-state system with the constant forces $\mathbf{X}_1, \mathbf{X}_2,\ldots,\mathbf{X}_k$ (k < m) corresponds to the state, where flows with the indices $j = k+1, k+2,\ldots, m$ disappear. The alternative statement of this law for continuum systems reads that in the stationary state compatible with the external constraints the dissipation function P is minimal:

$$P = \int T\sigma_s dV = \Sigma_j \int \mathbf{X}_j \mathbf{J}_j{}^{\mathrm{p}} dV = \min; \quad \delta P = 0. \tag{4.6.9}$$

This statement is usually substantiated involving linear phenomenological laws (4.4.1) and the Onsager's reciprocity relationships and is, therefore, considered valid for only the systems being in close proximity to equilibrium. From the positions of thermodynamics this law acquires a more general character. According to the evolution criterion (see 3.6.6) it is quite evident that if an external force prevents a system from reaching equilibrium, the system comes to a halt in the minimal-dissipation state. Using flow balance equation (2.4.8) the condition of inergy constancy for a stationary-state system may be written in the form:

$$dU_i/dt = -\int \mathbf{x}_i \cdot (\mathbf{j}_i{}^{\mathrm{e}} + \mathbf{j}_i{}^{\mathrm{p}}) dV = 0, \tag{4.6.10}$$

From this it directly follows that if some of the external flows $\mathbf{j}_i{}^{\mathrm{e}}$ supporting the stationary state ($\mathbf{x}_i$ = const) disappears ($\mathbf{j}_i{}^{\mathrm{e}} = 0$), the subscript-similar relaxation flow $\mathbf{j}_i^p$ also disappears along with the associated component of the dissipation function *P*. This statement does not depend on character of the phenomenological laws and is so evident that hardly needs some theorems to be proved.

Thus all basic statements of the current linear TIP may be obtained as deductions of thermodynamics without appeal to whatever postulates and hypotheses. This makes superfluous formulating complicated balance equations for mass, charge, momentum, energy and entropy, which has always been the most time-consuming part of the theory. It is not less important that such an approach excludes the necessity for preliminary and thorough knowledge of a number of fundamental disciplines to formulate the balance equations. This allows one to solve problems being not overburdened with hardened paradigms and dogmas associated with these problems. Furthermore, this approach opens up new possibilities to subsequently overcome the profound narrowness of non-equilibrium thermodynamics that is restricted to only linear systems and close-to-equilibrium states.

Chapter 5

HEAT-MASS TRANSFER THEORY

The development of the theory of irreversible processes (TIP) has created the prerequisites for a cardinal rapprochement between thermodynamics and the heat-mass transfer theory. Firstly, this theory has from the very beginning operated with the heat-mass transfer concepts: fields (both stationary and non-stationary), energy flows (including heat), gradients of potential (temperature), uniqueness conditions, etc. Secondly, thermokinetics is based on the equations of a more general form, from which the equations of heat conductivity, electric conductivity, diffusion, etc. ensue as a particular case. Thirdly, it also uses the balance equations for extensive values and expresses their sources in terms of the measurable parameters of a system. In a word, the TIP already contains the whole arsenal of tools necessary to describe and investigate the heat-mass transfer processes. Thermokinetics spreads still further and allows obtaining all statements of this theory essentially from thermodynamic. Therefore the TIP fundamental principles, laws and equations are most advisable to be stated from the positions of thermokinetics.

5.1. Elimination of Strange Delimitation of Thermodynamics and the Heat Exchange Theory

No sooner had the heat theory appeared, it immediately separated into two directions. In 1822 a known J. Fourier’s work appeared, which laid the foundation of the heat transfer theory; in 1824 not less famous S Carnot’s work laid the foundation of thermodynamics. Both works were based on the afterward-rejected theory of thermogen as the indestructible fluid, both considered temperature as some potential which gradient conditioned the heat transfer direction or conversion of heat into ordered forms of energy. However only Fourier operated with time as a physical parameter, and that left an imprint on the whole further development of those theories. The concept of entropy introduced by R. Clausius in 1850-1865 as the coordinate of reversible heat exchange and the S. Carnot's method of reversible cycles widely used in thermodynamics connected thermodynamics for a long time with the concept of equilibrium and quasi-static character (infinitesimal rate) of processes under investigation as the condition of their reversibility. A lot of time had passed before it became evident that "timeless" thermodynamics (to Brayan's locution) was substantially thermostatics.

Meanwhile the J. Fourier's ideas were running their course. Yet in 1822 the L. Navier's work appeared having laid the foundation of hydrodynamics of viscous liquids, G. Ohm derived his famous law in 1827, A. Fick set forth the diffusion equation in 1855. Those equations and the like described kinetics of momentum, charge, substance, etc. transfer. However both directions mentioned developed quite independently without any points of contacts. Their difference showed not only in terminology, but it rather rooted in a basic methodological nature. Carnot-Clausius' thermodynamics maintained aloofness from the transfer ideas and the heat exchange rate concept. The heat exchange theory, on the contrary, had nothing to do with the conversion of heat into other forms of energy and considered entropy as an extraneous concept. The so "fancy separation of two directions within the same area in macroscopic physics" (to K. Denbigh's locution) was too hard to be overcome by the TIP as well. Even today the definition of heat concept remains different in thermodynamics and the heat exchange theory. In thermodynamics this is the part of energy exchange caused by exclusively the temperature difference between bodies and not associated with substance exchange between them (Thermodynamics. Terms, 1973). The heat exchange theory, on the contrary, considers heat as the part of internal energy associated with random motion (because a system can exchange just what it has) and studies, along with heat conductivity, the heat transfer carried out by substance and enabled by heterogeneity of the fields of other physical values (Heat Transfer. Terms, 1980). Such a situation demands searching more cardinal means to unify the two said fundamental disciplines.

5.2. Conductive Heat Exchange (Heat Conductivity)

The heat exchange processes may be classified into three classes: conductive, convective and radiant heat transfer. The conductive heat transfer (heat conductivity) features the absence of observable (macroscopic) motion in a heat conductive medium with direct contact between bodies or parts of a body having different temperatures. The basic law of heat conductivity was stated, as it has been already mentioned, by J. Fourier having proceeded from interpreting heat as the indestructible fluid.

According to this law the heat flow density $\mathbf{j}_q$ is directly proportional to the temperature gradient ∇T reversed in sign:

$$\mathbf{j}_q = -\lambda\nabla T, \qquad (5.2.1)$$

where λ (W/m·K) – proportionality factor named coefficient of heat conductivity.

Classic thermodynamic interprets the heat flow as a conductive (not associated with the substance transfer) flow of the internal energy u with the density $\mathbf{j}_q$. Here the coordinate of a heat transfer process is construed as the entropy S. Therefore it is more correctly, from the positions of thermokinetics, to refer to rather the entropy flow with the density $\mathbf{j}_s = \mathbf{j}_q/T$ than to a heat flow. In this case Fourier's law for stationary heat conductivity directly ensues from kinetic equations (2.6.11) written down in the local form:

$$\mathbf{j}_s = L_s\mathbf{x}_s\,, \qquad (5.2.2)$$

where $\mathbf{x}_\text{s} = -\nabla T$ – motive force of the process; $L_s = \lambda/T$ – coefficient that should be rather named coefficient of *entropy conductivity*. Note that the "thermokinetic" form of heat conductivity law representation (see 4.3.1) is much closer to the original form (see 4.3.1) than the one ensuing from Osager's laws, where the thermodynamic force is used in the form of $\mathbf{x}_q = -T^1\nabla T$ or $\mathbf{x}_q = \ln T$ even when choosing the heat flow $\mathbf{j}_q$ as the generalized rate of the process.

The differential equation of non-stationary heat conductivity ensues from thermokinetics equally as directly. It is enough just to use the balance equation for the arbitrary field specific value θ_i of generalized form (4.3.1) assuming there $\theta_i \equiv u$ and $\sigma_i \equiv \sigma_q/T$. Using the definition of the specific heat at constant volume (isochoric) $c_\upsilon \equiv \partial u/\partial T$ in the absence of mass transfer and work (i.e. at constant ρ и c_υ) one can find:

$$\rho c_\upsilon\partial T/\partial t + \nabla\cdot\mathbf{j}_q = \sigma_q\,. \qquad (5.2.3)$$

This expression is the most general form of the differential equation of heat conductivity valid for both linear and non-linear processes. It is available in a more ordinary form if considered jointly with (6.2.1) assuming constant λ and introducing, to shorten the formula, the thermal diffusivity $\alpha_q = \lambda/c_\upsilon\rho$:

$$\partial T/\partial t = \alpha_q\nabla^2 T + \sigma_q/\rho c_\upsilon\,. \qquad (5.2.4)$$

This equation relates the heating rate of a body directly proportional to the temperature field and heat sources in it. The latter is very important as allowing for chemical reactions running in a heat-conductive medium (see 4.1.3), high-frequency and induction (eddy-current) heating, friction, etc., i.e. the availability of any entropy sources σ_s.

Just like other differential equations of thermokinetics, expressions (5.2.3) and (5.2.4) describe the entire group of the like phenomena. To extract a process under investigation from this entity and to completely describe it mathematically, it is necessary to take into consideration particular properties of the object. These are defined by uniqueness conditions including for a general case of non-stationary processes the initial, geometrical, physical and boundary conditions (including the initial temperature distribution, body configuration and size, body thermo-physical properties, surrounding relations, etc.). The problem thus stated is solved by either analytical, or numerical, or theoretical-experimental methods with an appeal to the heat exchange phenomena similarity theory. These methods are considered in special disciplines (A. Lykov, Y. Mikhailov, 1963).

5.3. Convective Heat Exchange

Convective heat exchange (or heat transfer) is usually understood as a heat exchange between a moving medium and a stationary one without a substance exchange between them. This process is always accompanied by heat conductivity dominating nearby the stationary surface. Therefore the basic law of convective heat exchange may be derived based on the same kinetic equations of thermokinetics in the form of (6.2.2) substituting herein the coefficient of heat conductivity λ for some empirical value α multiplied by the thickness $\delta_т = \Delta n$ of the thermal boundary layer of liquid (i.e. the liquid layer within which the liquid temperature varies from the wall temperature T_c to the temperature T_w of the bulk liquid flow). Taking into account that in stationary conditions $T_w = T_w(\mathbf{n})$, i.e. depends on only the normal coordinate $\mathbf{n}$ to the heat exchange surface, and substituting on this basis $\nabla T \equiv \partial T_w/\partial \mathbf{n}$ for $dT_w/d\mathbf{n}$ expression (5.2.1) may be represented thru separation of variables in the form:

$$dT_w = (\mathbf{j}_q \delta_T/\alpha_q)d\mathbf{n}. \tag{5.3.1}$$

Integrating this with respect to $\delta_т$ one can find:

$$\mathbf{j}_q = \alpha_q \, \Delta T, \tag{5.3.2}$$

where $\alpha = \lambda/\delta_т$ (W/m^2·K) – proportionality factor having been referred to as heat transfer coefficient; $\Delta T = (T_w - T_c)$ – thermal head. The further problem comes down practically to the definition of how this coefficient depends on various factors, viz. liquid properties, liquid flow pattern, body configuration and streamline, etc.

Differential equation of convective heat exchange may be found in the same way as expression (5.2.3). It is only necessary to take into account that the temperature of a moving liquid is a function of not just time, but also the coordinate **r** of this liquid, i.e. $T_w = T_w(\mathbf{r}, t)$. Therefore its total variation in the time domain dT_w/dt, along with the local variation $\partial T/\partial t$, includes the so-called convective variation $(\partial T/\partial \mathbf{r})d\mathbf{r}/dt = \nabla T\cdot\mathbf{v}$, defined by the flow velocity **v**. Allowing for this component equation (5.2.3) assumes the form:

$$dT_w/dt = \mathrm{a}_q\nabla^2 T + \sigma_q/\rho c_\mathrm{v}\,. \qquad (5.3.3)$$

This equation is usually named differential equation of energy in order to distinguish it from the other differential equation characterizing the heat exchange conditions at the wall–moving liquid interface. To derive this equation, let us heed the fact that there is a thin layer of stationary liquid nearby the wall ($n = 0$), wherein the heat transfer is provided by exclusively heat conductivity. Therefore, along with (53.2), one can write $\mathbf{j}_q = -\nabla T_{n\,=\,0}$, wherefrom it directly follows:

$$\alpha_q = -\lambda\nabla T_{n=0}\,/\,\Delta T. \qquad (5.3.4)$$

This is the differential equation of heat exchange manifesting that convective heat exchange so many times exceeds heat conductivity in intensity, as temperature gradient in the boundary layer exceeds thermal head in value.

5.4. Radiant Heat Exchange

Radiant heat exchange is usually understood as a heat exchange thru radiation and absorption of electromagnetic waves within thermal-frequency range by bodies separated with a transparent medium. This range is small and corresponds to waves with a wavelength of 0.8 micron thru 0.8 mm. Generally speaking, the radiation is an ordered (directional) process pertaining to one of the useful work categories. This is confirmed by the fact that the absorption of the radiant energy is accompanied by photosynthesis of organic compounds, ionization, dissociation, photo-effect, and the like phenomena. Therefore it makes sense to refer to the radiant heat exchange providing a radiant energy dissipation process occurs. This dissipation of electromagnetic energy takes place, generally speaking, not only in bodies themselves, but also in the medium separating them. Therefore it should be advisably considered as a “photon heat conductivity” phenomenon (G.F. Muchnik, I.B. Rubashov, 1974). Thus the differential form of the radiant heat exchange law may be obtained based on the same kinetic laws of thermokinetics in the forms of (2.6.10) and (2.6.11). In the last case the law may be written as:

$$\mathbf{j}_q = \lambda_f \nabla T, \tag{5.4.1}$$

where λ_f – coefficient of "photon heat conductivity". For optically dense media this coefficient is defined by the Henzel equation:

$$\lambda_f = 16\, k_б\, T^3/3æ_г\,, \tag{5.4.2}$$

where $æ_г$ – absorption factor of a medium.

For the stationary heat exchange ∇T may be represented, as shown above, in the form of the fraction $dT/d\mathbf{n}$. Separating on this basis the variables in (5.4.1) and integrating this expression with respect to the ray path length ℓ in-between the bodies with temperatures T_1 and T_2, one comes to the radiant heat exchange law expressed as:

$$j_q = [k_б/(1+ æ_г\ell)]\,(T_1^{\,4} - T_2^{\,4})\,. \tag{5.4.3}$$

This expression is a good approximation for media with low optical density (weak absorption).

Thus all integral and differential equations of the heat exchange theory may be derived from thermokinetics. This is what provides a methodologically unified approach to thermodynamics and the heat exchange theory.

5.5. Heat - Mass Exchange in Open Systems

Classic thermodynamics is known to have always distinguished only two kinds of system–environment energy exchange, viz. heat exchange and work. The former has been considered as a random form of energy supply, whereas the latter – as its ordered form. We owe the application of the thermodynamic method to open systems with mass transfer therein to J. Gibbs, who introduced the parameters M_k and N_k as additional independent state variables and derived the joint equation of the first and second laws of thermodynamics for open systems in the form of relationship (5.5.1) which can be more conveniently expressed in terms of the mole numbers of the k^{th} substances:

$$dU = TdS - pdV + \Sigma_k\, \mu_k\, dN_k\,, \tag{5.5.1}$$

where U, S, V – internal energy, entropy and volume of a system, respectively; T, p – absolute temperature and pressure, respectively; $\mu_k \equiv (\partial U/\partial M_k)_{S,V,Nm}$ – component potential determined at constant S, V and mole numbers of all other components N_m *mass transfer* process involving a variation of the system composition due to the k^{th} substances transfer across the system borders and from the *mass transfer* process involving the substance transfer without system composition variation.

The last term in this expression, by Gibbs' assumption, characterizes an independent process irreducible to heat exchange and cubic strain and involving a composition and mass variation for a system as a whole. He also assumed that the term TdS still (as in closed systems) characterized the elementary heat exchange $đQ$. In fact, he writes, "…if a system consists of parts supposedly not thermally interconnected, then any entropy reduction in either of these parts should be deemed impossible since such variations can not occur without heat transfer". However, as investigators were striking into the issue, they clarified the necessity to exclude from the total entropy dS and volume dV variations for open systems a part caused by the k^{th} substance transfer. Despite the existing disagreement in identification of this part (S.R. De Groot, R. Mazur, R. Haase, 1967), the great majority of investigators have come to construing the heat exchange and work in open systems as the part of energy exchange caused by exclusively the temperature gradient and not associated with the substance transfer across the system borders. In the same way heat is understood and referred to in the collection of terms recommended by the Academy of Science, "Process heat is the energy transferred at interaction from a one body to another depending on exclusively temperature of the bodies and not associated with substance transfer between them" (Thermodynamics. Terms, 1973).

To confirm the validity of such an approach, let us proceed from the joint equation of the first and second laws of thermodynamics derived for one mole of the pure k^{th} substance and, therefore, valid for both closed and open systems. Designating the molar energy, entropy and pure substance volume as u_{ko}, s_{ko} and υ_{ko}, respectively, and considering them as temperature and pressure functions ($s_{ko} = s_{ko}(p,T)$, $\upsilon_{ko} = \upsilon_{ko}(p,T, r_k)$) the joint equation of the first and second laws of thermodynamics has the form:

$$du_{ko} = đq_k - đw_k = Tds_{ko} - pd\upsilon_{ko} \,. \qquad (5.5.2)$$

Here $đq = Tds_{ko}$, $đw = pd\upsilon_{ko}$ – elementary neat and expansion work of an open system under consideration.

Multiplying all terms of this equality by the mole number of the k^{th} substance and applying the Legendre transformation $N_k du_{ko} = dU_{ko} - u_{ko} dN_k$, equation (6.2.2) may be modified as:

$$dU_{ko} = đQ_k - đW_k + u_{ko}dN_k, \qquad (5.5.3)$$

where $đQ_{ko} = N_k đq_{ko} = N_k T ds_{ko}$ and $đW_{ko} = N_k đw_{ko} = N_k p d\upsilon_{ko}$ – respectively, elementary heat exchange and expansion work of the same pure k^{th} substance taken to the amount of the N_k moles if the heat and work concepts maintain their classic meaning. It is easy to see that once the terms TdS and pdV in Gibbs' relationship (5.5.1) are still understood as the heat exchange $đQ$ and expansion work $đW$, then in a particular case of a single-component system ($s_k = s_{ko}$; $\upsilon_{ko} = \upsilon_{ko}$; $u_k = u_{ko}$ и $\mu_{ko} = u_{ko} - Ts_{ko} + p\upsilon_{ko}$) this relationship does not go over into (5.5.3) as should be expected. Hence the terms of (5.5.1) do not characterize independent processes as Gibbs assumed and the principle of effect distinguishability demands, while the term $\Sigma_k \mu_k dN_k$ does not determine the energy exchange caused by the k^{th} substance transfer across the system borders.

Thus there arises a problem in open systems how to distinguish the heat transfer, work and mass transfer. The decision to the problem supposes finding such coordinates of these processes which remain independent from processes of other kind simultaneously running. It is quite evident that the total entropy S and the total volume V of an open system are not any more coordinates of heat transfer and expansion work therein since they vary at mass transfer as well (variation of the total number of moles N at constant composition of the system). The specific entropy $s = \Sigma_k s_k r_k$ and specific volume of the mixture $\upsilon = \Sigma_k s_k r_k$ are not these coordinates either since they vary even at $N =$ const due to the system composition variation (variation of the mole fractions r_k of the k^{th} components). The partial molar entropies s_k and the volumes υ_k of the k^{th} components can not either serve as coordinates of heat transfer and work in open systems since they vary with the variation of relationship between the mole numbers N_k of the k^{th} substances, i.e. $s_k = s_k(p,T, r_k)$ и $\upsilon_k = \upsilon_k(p,T, r_k)$ [1]. Lastly, not quite adequate are the coordinates $s_{ko}(p,T)$ and $\upsilon_{ko}(p,T, r_k)$ since they do not allow for the heat and bulk effects arising at the irreversible mixing of the introduced component with the substance of the system. Thus the concepts of "heat" and "work" loose their intrinsic meaning in the systems where diffusion takes place (M. Tribus, 1970). In this connection the classic division of the external energy exchange into heat transfer and work looses its heuristic value and should give place to other process classification having nothing to do with the energy exchange means. Such is, in particular, the "heat process" featuring a temperature variation in a system at constancy of its volume, mass and composition irrespective of what causes the process – external heat

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[1] Remember that partial molar function of the k^{th} substance means an increment in adequate extensive value when introducing into the system one mole of this substance at constant temperature, pressure and other potentials.

exchange or internal heat sources. A coordinate of this heating process may be the entropy of a mixture irreversibly composed $S^o = \Sigma_k N_k s_{ko}$ (in the absence of the heat mixing processes), where s_{ko} is considered a function of exclusively intensive parameters (temperature and pressure as the simplest case). Then:

$$đQ = \Sigma_k N_k T ds_{ko} = T d_\Theta S^o, \tag{5.5.4}$$

where $d_\Theta S^o$ – part of the entropy variation caused by exclusively heating and not associated with the system volume and coordinate variation (including N_k). This heat keeps the same meaning as in classic thermodynamics, i.e. is defined by internal energy variation in the system at constancy of its volume V and the coordinates $\mathbf{Z}_i$ of all other kinds of work ($đQ = [dU]_{V,\mathbf{Z}_i}$). It is easily seen that the heat Q absorbed or released by the body is defined in this case in terms of the "isocoordinate heat capacity" $C_\Theta = (\partial U/\partial T)_{V,\mathbf{Z}_i}$ of the system, which is a conceptual generalization of the isochoric heat capacity C_V for the case of a polyvariant system. Since the derivatives of some parameters of the system (U in this case) with respect to its other parameters (T in this case) are also its state parameters, the system isocoordinate heat capacity C_Θ becomes state parameter (like C_V), while the heat $đQ$ – measure of internal heat energy variation:

$$đQ = dU_{\text{т}} = C_\Theta dT. \tag{5.5.5}$$

Similarly the expansion work for an open system $đW_p$ may be found as:

$$đW_p = \Sigma_k N_k p d\upsilon_{ko} = p d_\psi V^o, \tag{5.5.6}$$

where $V^o = \Sigma_k N_k \upsilon_{ko}$ – volume of a reversibly composed mixture (in the absence of the bulk mixing effects); $d_\psi V^o$ – volume variation due to exclusively bulk deformation of the system components and not associated with the system intensive parameters' variation ψ_i (including p, T and c_k).

The above proposed definition of heat and work in open systems as notions keeping their classic meaning corresponds to the axiom of process distinguishability and allows to distinguish these processes as independent (irreducible to each other). In this case the heat-mass exchange process should be first of all distinguished from the diffusion process of the k^{th} substances across the system borders, which involves the variation of system composition with the system mass invariable. Accordingly, the *heat-mass exchange* will be construed as an exchange of internal heat energy between bodies if caused by the substance transfer across the system borders and having nothing to do with the variation of the system composition.

It is easy to see that the term TdS in relation (5.5.1) includes the component $\Sigma_k Ts_{ko} dN_k$ caused by the transfer of the pure k^{th} substances across the system borders. This is the component that ought to be construed as the analytical expression of the heat-mass exchange $\text{đ}Q_m$:

$$\text{đ}Q_m = \Sigma_k Ts_{ko} dN_k\,. \qquad (5.5.7)$$

Similarly, the term pdV in open systems, along with the usual expansion work $\text{đ}W_p = \Sigma_k N_k p d\upsilon_{ko}$, also includes the so-called "input work" $\text{đ}W_{in} = \Sigma_k p\upsilon_{ko}\, dN_k$:

$$\text{đ}W_{in} = \Sigma_k p\upsilon_{ko}\, dN_k. \qquad (5.5.8)$$

Substituting (5.5.7) and (5.5.8) into the Gibbs relation (5.5.1) gives:

$$dU = \text{đ}Q + \text{đ}Q_m - (\text{đ}W_p + \text{đ}W_m) + \Sigma_k\, \mu_k\, dN_k\,. \qquad (5.5.9)$$

From this it follows that the term $\Sigma_k \mu_k dN_k$ in the Gibbs relation characterizes the heat-mass exchange with the diffusion of the k^{th} non-reacting substances across the system borders $\text{đ}U_d$. This process should be called the *diffusion energy-mass exchange* 1), unlike the diffusion in its exact meaning. In such a case the total energy-mass exchange $\Sigma_k u_{ko} dN_k$ can be represented as an algebraic sum of the heat-mass exchange $\text{đ}Q_m$, the input work $\text{đ}W_{in}$ and the diffusion energy-mass exchange $\text{đ}U_d$.

Thus the heat exchange in open systems includes the conductive and convective components of the heat flow caused by the heat conduction $\mathbf{j}_q^{\,c}$ and the heat-mass exchange $\mathbf{j}_q^{\,k}$, respectively. The latter is inseparable from the density of the k^{th} substance flow across the system borders $\mathbf{j}_k = \rho_k \mathbf{v}_k$ (mol/m^2·s) and according to (5.5.4) equals $\mathbf{j}_q^{\,\kappa} = Ts_{ko}\, \text{j}_k$. Then the basic law of heat exchange in open systems becomes:

$$\mathbf{j}_q = -\lambda \nabla T + \rho_k\, Ts_{ko}\, \mathbf{v}_k\,. \qquad (5.5.10)$$

This expression fundamentally differs from that traditionally used in the heat-mass exchange theory because it contains not the enthalpy h_k of the k^{th} substance input having nothing to do with the internal heat energy of the substance, but the associated energy Ts_{ko} of the substance input.

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1) The term "diffusion" (from the Latin "diffusio" – spreading) relates, strictly speaking, to the other process – the equalization of the component concentrations all over the bulk of the system with its composition and mass invariable.

Conclusion to Part 2

As mentioned in this section, all the basic integral and differential equations of classic and nonequilibrium thermodynamics, as well as of the heat-mass exchange theory, can be obtained as consequences from thermokinetics without any recourse to whatever hypotheses, postulates and statistical-mechanical considerations. Thereby not only the methodological principles of the thermokinetic construction acquire a reliable substantiation, but also the basic laws these disciplines state. Then the assumptions which underlie some theory or other become clearer, as well as the applicability limits of the basic concepts and principles pertaining to these theories.

The deductive interpretation of the heat engineering theoretical grounds eliminates the strange historical delimitation of various branches in the heat doctrine and restores merits to thermodynamics as a consistently phenomenological theory, which consequences have the status of oracles. It is not less significant that such an interpretation gives the crux of the matter in the most concise and compact form free of the burden of historical accretions. Besides, the synthesis of the heat engineering theoretical grounds on a unitary methodological basis exposes the reserves for their further generalization. All this essentially improves the thermodynamic investigation method in its heuristic value.

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 thermokinetics 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 6

CORRECTION OF THERMODYNAMICS OF OPEN AND POLYVARIANT SYSTEMS

Classic thermodynamics in accordance with the equilibrium self-non-disturbance 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, meantime, 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 k^{th} 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 k^{th} 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 k^{th} 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 thermokinetics enabling consideration of internal processes in isolated systems not recurring to the formalism above described.

6.1. 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 sys-

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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 k^{th} substances across the system borders). Therefore hereafter we will distinguish the diffusion in a strict meaning of this word from the selective.

tems doing other kinds of work beside expansion work the authors of many guidelines in thermodynamics express this equation as:

$$dU = \Sigma_i \Psi_i \, d\Theta_i \,, \quad (i = 1,2,\ldots,n) \tag{6.1.1}$$

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 (6.1.1) is often applied to the analysis of surface phenomena representing work as (V. Sychev, 1986):

$$đW_f = \sigma_f df \,, \tag{6.1.2}$$

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:

$$đW_f = (p' - p'')\mathrm{d}V' \,, \tag{6.1.3}$$

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 (6.1.1) 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:

$$đW_\ell = F_\ell d\ell \,. \tag{6.1.4}$$

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: $d\ell' \le 0$, $d\ell'' \ge 0$). Therefore the work to extend the rod actually refers to the terms of the second sum in (2.2.5), which have vector nature:

$$\text{đ}W_\ell = \mathbf{F}_\ell'\cdot d\boldsymbol{\ell}'/2 + \mathbf{F}_\ell''\cdot d\boldsymbol{\ell}''/2 = \mathbf{F}_\ell\cdot d\boldsymbol{\ell}\,. \qquad (6.1.5)$$

It comes down even so far that equation (6.1.1) 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, $\boldsymbol{R}_i$ and $\boldsymbol{\varphi}_i$ types to be generally introduced. However, 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 i^{th} 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 $\text{đ}W_i^{\text{dis}}$ may be herein expressed as:

$$\text{đ}W_i' = \Psi_i' d_e\Theta_i'\,;\ \text{đ}W_i'' = \Psi_i'' d_e\Theta_i''. \qquad (6.1.6)$$

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 k^{th} 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 k^{th} 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 k^{th} 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 – *disordered work* (failing a more adequate term) and denote them as W_i^{dis}.

Work of quite other kind is done when the elementary forces $\mathbf{F}_{ik}$ cause the same-sign displacement $d\mathbf{r}_{ik}$ of the objects these forces are applied to, i.e. the work has an ordered directional character. In this case $\mathbf{\Sigma}_k\,\mathbf{e}_{ik} \neq 0$, and the forces $\mathbf{F}_{ik}$ have a resultant $\mathbf{F}_i$ even though the system remains homogeneous. Such is the work done by technical devices (machines) intended for the purposeful conversion between kinds of energy. Therefore such work is often named *technical* (A.I. Andrushchenko, 1975). However, the work of such kind is generally done by not only mechanical devices, but also biological, chemical, astrophysical, etc. systems. Therefore from the positions of thermokinetics this should be preferably referred to as the *useful* or *ordered* work W_i^e.

The useful work is also done when the system is heterogeneous, but the forces $\mathbf{F}_{ik}$ are applied to subsystems with different signs of the Θ_{ik} property, e.g. to positive and negative charges, north and south poles of magnetic dipoles, electrons and holes in metals, zones with a reduced and increased (as compared with average) density of the Θ_i parameter, etc. Such kind of work is done at the dielectric and magnetic polarization, gas dissociation and ionization, rod extension, redistribution of charges, substances, momentums and entropy between the parts of an intrinsically homogeneous system. Dividing for such a case the sum $\mathbf{\Sigma}_k\Theta_{ik}\mathbf{e}_{ik}$ into two parts having the same sign of the Θ_{ik} and $\mathbf{e}_{ik}$ values the resultant force $\mathbf{F}_i$ other than zero is again received. As shown in Chapter 2, coordinates of such kind processes (i.e. parameters necessarily varying when the process running) are the "displacement vectors" $\Delta\mathbf{R}_i$ or the "distribution moments" $\mathbf{Z}_i = \Theta_i\Delta\mathbf{R}_i$ relating to, respectively, the resultant forces $\mathbf{F}_i$ or their specific values $\mathbf{x}_i = \mathbf{F}_i/\Theta_i = - \nabla\psi_i$ (thermodynamic forces). The analytical expression for the useful work W_i^e in a steady process (where $(d\mathbf{R}_i\cdot\nabla)\psi_i = d\psi_i$) may, according to (2.2.9), obtain a more simple form as:

$$W_i^e = \int \mathbf{X}_i\cdot d\mathbf{Z}_i = - \int \Theta_i d\psi_i = - \Theta_i(\psi_i'' - \psi_i'), \qquad (6.1.7)$$

where ψ_i', ψ_i'' – generalized potential for the energy carrier Θ_i entering the system and leaving it, respectively.

As can be seen, the useful work is associated with the variation of this kind energy value $U_i = \Theta_i\psi_i$ when the energy carrier crosses the system borders, i.e. with the conversion of energy from one form into other. Therefore the useful work is a *quantitative measure of energy conversion*. This kind of work features an *ordered* (vector) character.

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 (2.6.2) and (2.6.3), according to which:

$$đW^{dis} = - \Sigma_i \int \mathbf{j}_i^p\cdot\nabla\psi_i dV = \Sigma_i \int \psi_i\sigma_i \, dV, \qquad (6.1.8)$$

where $\mathbf{j}_i^r$ – relaxation component of the i^{th} 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) $W_k^{\text{dif}} = \Sigma_k\int w_k dP_k$, the material destruction work $W_d^{\text{dis}} = \int \sigma_f df$ 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 fact that the experimental values of the useful work done in chemical reactions conform to the analytical values of the same calculated by the free energy decline promotes to a considerable degree the incomprehension of the fundamental difference between the augend and the addend in expression (2.2.5). Such conformity is not accidental since dissipation heat is equivalent to useful work. Therefore the incorrectness of such authentication is completely expressed in only the conclusion of the "complete convertibility" of any kind of work (J. Szargut, R. Petela, 1968). In this respect thermokinetics is remarkable in that it explicitly reveals the specific character of the augend and the addend of (2.2.5). This specificity is that the addend's terms have the tensor order different from that of the augend's terms. Physically this means that vector processes remain *internally non-equilibrium* even being quasi-static (infinitely slow). This situation is absolutely extraneous to classic thermodynamics where the adjectives quasi-static and reversible have always been synonyms. Non-equilibrium processes naturally demand for their description specific non-equilibrium parameters to be introduced unavailable in equation (6.1.1) and extraneous to classic thermodynamics in principle. Their absence forces to refer the vector processes of polarization, magnetization to just a category of "other kinds of work" done by a polyvariant system. This has the result the investigator does not distinguish the ordered and disordered forms of external action on a system. Here the incomprehension roots that 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 $\bar{U}(\Theta_i)$.

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rameters to be introduced unavailable in equation (6.1.1) and extraneous to classic thermodynamics in principle. Their absence forces to refer the vector processes of polarization, magnetization to just a category of "other kinds of work" done by a polyvariant system.

One of such errors consists in a deep-rooted belief that homogeneous systems are as well capable for useful work. In the homogeneous isobaric-isothermal chemical reactions this work is numerically expressed in terms of the Gibbs' energy decline $G = U + pV - TS$. In reality the useful work in chemical reactions can be done if only the chemical potential gradients are available, which demands a spatial division of the reagents. This is what occurs in Van't Hoff's box, galvanic or fuel cells. The homogeneous chemical reactions inevitably become irreversible and involve the dissipation heat release, which is allowed for in TIP by an adequate increment in entropy (4.3.3).

6.2. Substantiation of Second Law Applicability to Non-Heat Engines

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

$$\eta_j = W_j / W_i = 1. \qquad (6.2.1)$$

Here W_j – work done by a non-heat engine; W_i – energy U_i' 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 k^{th} 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:

$$dU_i = \Psi_i \, d\Theta_i \,. \; (i = 1, 2, \ldots, n) \tag{6.2.2}$$

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 k^{th} 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

$$W_{\text{ц}} = \oint \psi_i d\Theta_i \tag{6.2.3}$$

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 (6.7.2) 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 (6.7.2) 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 :

$$\text{đ}W_j = (\overline{\psi}_i' - \overline{\psi}_i'')d\Theta_i' \text{ или } W_j = (\overline{\psi}_i' - \overline{\psi}_i'')\Theta_i^* \,. \tag{6.2.4}$$

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 (3.2.3):

$$\eta_j = W_j / U_i' = 1 - \overline{\psi}_i'' / \overline{\psi}_i' . \qquad (6.2.5)$$

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 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 $\text{đ}W_e = d(U_e' - U_e'') = (\varphi' - \varphi'')d\Theta_e$, which in relation to the well energy loss dU_e' gives the part

$$\eta_j = 1 - \varphi''/\varphi', \qquad (6.2.6)$$

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 $\text{đ}W_p^e = (p' - p'')dV$, 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 (6.7.5). 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 k^{th} 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 $\text{đ}W_k = d(U' - U'') = (h_k' - h_k'')dN_k$. 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):

$$\eta_i = 1 - h''/h' , \qquad (6.2.7)$$

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 $\Theta_i^*=\Delta\Theta_i''$ 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 $đW_g = (\psi_g' - \psi_g'')dM_1$. 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 (6.7.5). 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 (6.7.7).

Thus the laws of energy conversion in any unordered form appear to be unitary 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. 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 $\Delta\Theta_\mathrm{e}$ 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 $dU_\mathrm{e}' = \Psi_i d\Theta_i$ supplied to the converter appears to be identical with the useful work $\text{đ}W_\mathrm{e} = (\varphi' - \varphi'')d\Theta_\mathrm{e}$ 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 nonequilibrium 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 (6.7.9), 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 i^{th} energy carrier. This is what means the "compensation", which necessity R. Clausius has stated. In this case the work W_i^{e} according to (6.7.4) makes up relative to the supplied energy $U_i' = \psi_i'\Theta_i$ the same part (6.7.5) 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 (6.7.5) 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:

$$\eta_i = W_i/\Sigma_j U_i' \,. \tag{6.2.8}$$

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 i^{th} 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.

6.3. Correction of Material Equilibrium Conditions

Based on relationships (5.5.1) Gibbs was he first who defined the conditions of equilibrium distribution of the k^{th} substances in heterogeneous systems. Those conditions consisted in equality of temperatures T, pressures p and chemical potentials μ_k of the k^{th} 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 k^{th} 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 k^{th} 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 k^{th} substances is running, the thermal equilibrium can not be either reached since the heat-mass transfer (transfer of internal energy of k^{th} 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 $V = \Sigma_k N_k \upsilon_k$, nor the entropy $S = \Sigma_k N_k s_k$ particularly, being extensive values, do not remain, generally speaking, invariable with introducing the k^{th} 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 k^{th} substance should not vary the parameters s_{ko} and υ_{ko}. Therefore considering the internal energy of the k^{th} component U_k as a function of the independent variables s_{ko}, υ_{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:

$$dU = \Sigma_k N_k T ds_{ko} - \Sigma_k N_k p d\upsilon_{ko} + \Sigma_k \varsigma_k dN_k, \qquad (6.3.1)$$

where $\varsigma_k = (\partial U_k/\partial N_k)$ – potential of the k^{th} component corresponding to the osmotic diffusion of the k^{th} 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 k^{th} substance and the mixing processes involved. These effects are inseparable from the substance introduction and, therefore, refer to the last term of (6.3.1).

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 $\Sigma_k p\upsilon_{ko} dN_k$ from the first two of its components and simultaneously adding them to the last component (so that not to disturb the energy balance):

$$dU = \Sigma_k N_k T ds_{ko} -- \Sigma_k N_k p d\upsilon_{ko} + \Sigma_k (\mu_k + T s_{ko} - p\upsilon_{ko}) dN_k, \qquad (6.3.2)$$

wherefrom it follows that

$$\varsigma_k = \mu_k + T s_{ko} -- p\upsilon_{ko} = u_k - T(s_k - s_{ko}) + p(\upsilon_k - \upsilon_{ko}). \qquad (6.3.3)$$

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 k^{th} component υ_k ($\mu_k = u_k - T s_k + p\upsilon_k$) one can find that for not interacting substances ($s_k = s_{ko}$ and $\upsilon_k = \upsilon_{ko}$) 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 (6.3.1), unlike (6.2.1), changes to relationship (6.2.3) 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:

$$\zeta_k = (\partial U/\partial N_k)_{Sko,V,Nk}. \qquad (6.3.4)$$

This potential is advisably to be named diffusive. Its relation to the chemical potential may be revealed coordinating Gibbs' relationship (6.1.1) with new uniqueness conditions. Assuming in (6.1.1) $dV = 0$ and rearranging the term $\Sigma_k Ts_k dN_k$ gives:

$$dU = \Sigma_k N_k T ds_{ko} + \Sigma_k \zeta_k dN_k . \qquad (6.3.5)$$

where

$$\zeta_k = h_k + T(s_{ko} - s_k). \qquad (6.3.6)$$

In even more particular case, when the components do not interact and the partial molar enthalpy and entropy of the k^{th} 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:

$$dU = \Sigma_k N_k T ds_{ko} + \Sigma_k h_k dN_k . \qquad (6.3.7)$$

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}, υ_{ko} = const) using the method described in Chapter 4 one can find that the equilibrium distribution of the k^{th} 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:

$$\varsigma_k' = \varsigma_k''. \qquad (6.3.8)$$

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

$$\zeta_k' = \zeta_k''. \qquad (6.3.9)$$

At last, for a filtration process equilibrium occurs with the equality of enthalpies of the k^{th} substance in the system and filtrate:

$$h_k' = h_k'' . \qquad (6.3.10)$$

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 (4.4.1) 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 (Chapter 12).

6.4. Definition of Potential State Functions for 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. The reason of this becomes more explicit if approaching the question from the positions of thermokinetics. According to (2.5.6) the ynergy Y of any, including open, system, i.e. its reversible (capable for work) part, may be found both from the "reverse balance", i.e. by the difference between the system energy U and its equilibrium part $\Sigma_i\Psi_i\,\Theta_i$, and directly in terms of the non-equilibrium parameters $\mathbf{X}_i$ and $\mathbf{Z}_i$. At that according to (2.5.6)

$$\text{đ}W = -d(U - \Sigma_i\Psi_i\Theta_i) + \Sigma_i\Theta_i d\Psi_i\,, \tag{6.4.1}$$

where the expression in brackets defines the system ynergy E found from the "reverse balance". In the particular case of an open multi-component thermo-mechanical system described by Gibbs' relationship (6.1.1) expression (2.5.6) becomes:

$$\text{đ}W = -d(U - TS + pV - \Sigma_k\mu_k N_k) = SdT - Vdp - \Sigma_k N_k d\mu_k. \tag{6.4.2}$$

It may be easily confirmed applying to the terms of Gibbs' relationship (6.2.1) the Legendre transformation $TdS = dTS - SdT$; $pdV = dpV - Vdp$; $\mu_k dN_k = d\mu_k N_k - N_k d\mu_k$ followed by their rearrangement. Since there are no the $\mathbf{X}_i$ and $\mathbf{Z}_i$ parameters in classic thermodynamics, the open system free energy may be found from exclusively the reverse balance. In this case with the traditional definition of the chemical potential as $\mu_k \equiv u_k - Ts_k + pv_k$ the left-hand side of (6.4.1) becomes zero since $\Sigma_k\mu_k N_k = U - TS + pV \equiv G$. This is what the known Gibbs-Duhem relationship follows from:

$$SdT - Vdp - \Sigma_k N_k d\mu_k = 0. \tag{6.4.3}$$

Based on this, a conclusion is usually drawn that there is no the potential in thermodynamics of open systems, which reduction would define the work done by a system (I. Bazarov, 1991; G. Gladyshev, 1988).

The paralogism of the situation arisen is that open multi-component systems are actually capable for useful work. Such are, in particular, the fuel cells using chemical affinity of fuel components. However, this needs the components, e.g. oxygen and hydrogen, to be spatially separated and separately supplied to the fuel cell electrodes. In other words, a spatial heterogeneity of the system is required described in thermokinetics by the specific parameters $\mathbf{X}_i$ and $\mathbf{Z}_i$. In this case applying the Legendre transformation $\Psi_i d\Theta_i = d\Psi_i\Theta_i - \Theta_i d\Psi_i$ to (6.3.1) gives:

$$d(U - \Sigma_i\Psi_i\Theta_i) = dE = \Sigma_i\Theta_i d\Psi_i - \Sigma_i\mathbf{X}_i\cdot d\mathbf{Z}_i. \qquad (6.4.4)$$

Since in this equation the expression $\Sigma_i\Theta_i d\Psi_i$ representing Gibbs-Duhem relationship (6.4.3) in the brief form becomes zero, the sum of all kinds of useful works $\Sigma_i\mathbf{X}_i\cdot d\mathbf{Z}_i$ in an open system is defined by its ynergy reduction:

$$\text{đ}W = \Sigma_i\mathbf{X}_i\cdot d\mathbf{Z}_i = -\,dE\,. \qquad (6.4.5)$$

Thus the reason the Gibbs' free energy looses its potential properties is the said "under-determinacy" of open non-equilibrium systems, i.e. the attempt to investigate them with the same set of variables as in equilibrium thermodynamics. Here the imperishable advantage is rooted, which can be obtained from introducing the inergy as the most common measure of order and integrity of both open and closed, simple and complex, homogeneous and heterogeneous systems.

6.5. 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 $\text{đ}W$ go over into the inequalities:

$$\text{đ}Q \neq TdS\;;\; \text{đ}W_p \neq pdV, \qquad (6.5.1)$$

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

The intensity of processes increases, inequalities (6.5.1) 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 k^{th} substances into the system, work against surface tension forces, polarization and magnetization). In this case not only the masses M_k of the k^{th} 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 $đW_i^e$:

$$đU_k \neq \mu_k dN_k;\ đW_i^e \neq \mathbf{X}_i \cdot d\mathbf{Z}_i\,. \tag{6.5.2}$$

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 k^{th} substance masses, the volume, etc.) by the "sinks" $d_u\mathrm{R}_j$ 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 under-determinacy 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 $\mathbf{j}_i^{\mathrm{e}}$ 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:

$$d_e\Theta_i/dt = -\int \nabla\cdot\mathbf{j}_i^{\mathrm{e}}\, dV\,. \tag{6.5.3}$$

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 $N_i^{\mathrm{un}} = đW_i^{\mathrm{un}}/dt$), where ψ_i is a local value of the generalized potential on the system border:

$$N_i^{\mathrm{un}} = \int \psi_i \nabla\cdot\mathbf{j}_i^{\mathrm{e}}\, dV = \int \psi_i \mathbf{j}_i^{\mathrm{e}}\, df. \tag{6.5.4}$$

The flows $\mathbf{j}_i^{\mathrm{e}}$ 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 (quasi-static) state variations, i.e. to the so-called reversible processes. Then $\int \nabla\cdot\mathbf{j}_i^{\mathrm{e}} dV = d\Theta_i/dt$ and relation (6.5.4) is simplified going over into (2.3.2). Table 6.1 illustrates the exact analytical expressions for heat exchange, mass exchange, expansion work and other unordered works in reversible and irreversible processes as based on (6.5.4). All kinds of unordered works (including heat exchange and mass exchange) are assumed in the table as positive if augmenting the system energy.

Table 6.1

Exact Analytical Expressions for Unordered Works

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

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 k^{th} 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.

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}. 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 $\mathbf{j}_i^{\text{r}}$). However, it is rather problematic to distinguish the component $\mathbf{j}_{\text{i}}^{\text{e}}$ in the continuum bulk elements. Therefore, let us consider the possibility to simplify the terms of the second sum in this expression. To do so, it is necessary to take into consideration that the redistribution processes correspond to the development $\nabla\cdot(\psi_i\mathbf{j}_i^{\text{e}})$ at $\nabla\cdot\mathbf{j}_i^{\text{e}} = 0$. For the system as a whole this condition takes the form of $\int\nabla\cdot\mathbf{j}_i^{\text{e}}\,dV = 0$. Changing in this expression from the volume integral to the integral $\mathbf{j}_i^{\text{e}}\cdot\mathbf{n}\,df = 0$ taken through the closed surface f of the system gives that at $\mathbf{j}_i^{\text{e}} \neq 0$ this condition implies existing the parts f' and f''on this surface with the opposite sign of the product $\mathbf{j}_i^{\text{e}}\cdot\mathbf{n}$, i.e. existing the flows $\mathbf{j}_i'$ and $\mathbf{j}_i''$ entering the system and leaving it. Then:

$$\int\mathbf{j}_i\cdot\mathbf{n}\,df = \int\mathbf{j}_i'\cdot\mathbf{n}\,df' + \int\mathbf{j}_i''\cdot\mathbf{n}\,df'' = J_i'' - J_i' = 0, \qquad (6.5.5)$$

where $J_i' = \int\mathbf{j}_i'\cdot\mathbf{n}\,df' \leq 0$ and $J_i'' = \int\mathbf{j}_i''\cdot\mathbf{n}\,df'' \geq 0$ – energy carrier flows at the system inlet and outlet, respectively.

Thus, to distinguish in the balance equation (2.6.3) the flow external component J_i^{e} caused by the useful work W^{e} done from the relaxation component J_i^{r}, it is possible to proceed from the conservation of the energy carrier flows J_i' and J'' at the system inlet and outlet, respectively. Substituting into (2.4.7) the bulk element dV across the flow $\mathbf{j}_i^{\text{e}}$ as the product of its cross-section normal-to-flow vector element $d\mathbf{f}$ and the normal element $d\mathbf{n}$ ($dV = d\mathbf{f}\cdot d\mathbf{n}$) with $(d\mathbf{n}\cdot\nabla)\psi_i = d\psi_i$ for steady flow gives the following instead of the second sum in (2.4.7):

$$N_i = \int\left(\int \mathbf{j}_i^{\mathrm{e}} \cdot d\mathbf{f}\right) d\psi_i = -\int \mathrm{J}_i^{\mathrm{e}} d\psi_i = J_i^{\mathrm{e}}(\psi_i' - \psi_i''), \qquad (6.5.6)$$

where $J_i^{\mathrm{e}} = -\int j_i^{\mathrm{e}} \cdot df = J_i'' = -|J_i'|$ – energy carrier "transit" flow crossing the system without changing its value; ψ_i', ψ_i'' – energy carrier potentials at the system inlet and outlet, respectively.

Thus the useful component is associated with the energy carrier "transit" flow J_i^{e} which crosses a system without changing its value. This statement may be instantiated by the electric machine where input current is known to be equal to output one. This is the same evident fact for also the cyclic heat engine since in any cycle the entropy rise $\Delta S_{1\text{–}2}$ at heat supply from heat well is numerically equal to its loss $\Delta S_{2\text{–}1}$ at heat rejection to heat sink. Therefore, for steady state the entropy flows $J_s^{\mathrm{e}} = \Delta S/\Delta t$ at the machine inlet and outlet are the same, too. This is the circumstance that served for S. Carnot the basis to compare heat engine with mill wheel (hydraulic machine). The analytical equations derived from the above expression are for convenience tabulated in Table 6.2.

Table 6.2

Exact Analytical Expressions for Ordered Works

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

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 $\mathbf{j}_i^e$ across the system borders [1]. 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.

Besides, a comparison between Tables 6.1 and 6.2 shows 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.

6.6. Possible 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. 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.

It should be noted, however, that equilibrium thermodynamics considered the environment as a single equilibrium whole with no allowance for the temperature gradients occurred there. Besides, it considered the only cyclic heat engines. At such conditions the ban on using the dissipative heat from the environment directly ensued from the reasoning as described in Chapter 4 and was quite natural.

The situation radically changes with the world ocean temperature stratification considered. In this case using the ocean as a free energy (ynergy) source not only does not contradict thermodynamics, but also has been long used at the oceanic power stations. The similar situation takes place if non-heat and non-cyclic engines are considered as thermokinetics does.

Let we have an arbitrary flow-type machine converting the flow energy of some substance $J_m = dM/dt$, which chemical potential decreases from the value μ_1 at inlet down to μ_0 at outlet (at equilibrium with the environment). The work of such a machine according to (6.3.9) is equal to:

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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.

$$W_i^e = M^*(h_1 - h_0) - M^*(T_1 s_1 - T_0 s_0), \qquad (6.6.1)$$

where h_1, h_0; s_1, s_0; T_1, T_0 – enthalpies and entropies at machine inlet and outlet, respectively (at equilibrium with the environment); M^* – mass of the working medium passed thru the machine.

Providing the working medium expands reversibly and adiabatically ($s_1 = s_0$), the above expression may be written as the algebraic sum of two components:

$$W_i^e = M^*(h_1 - h_0) - S^*(T_1 - T_0), \qquad (6.6.2)$$

where $S^* = M^*s_1$ – entropy transferred by the substance flow thru the machine.

Here the first term of the right-hand side characterizes the work done by the substance flow at its enthalpy reduction, while the second one – the work done by the entropy flow at its temperature reduction. This means that the machine under consideration represents a combined engine with two interconnected flows of energy carriers $J_m = dM^*/dt$ and $J_s = dS^*/dt$, wherein both the intramolecular energy of the substance and its internal heat energy are converted. If the working medium of such a machine receives heat from the environment which temperature $T_1 > T_0$ and which is thus certainly capable for work toward the heat receiver, this naturally influences the receiver-done work. This is, e.g., the case with the Thomson's heat the thermo-element electrode absorbs when electric charge is moving therein, as well as with recovery plants using wasted heat of a relatively low (as compared with the heat source) potential. Whatever violations of thermodynamic laws are naturally absent in this case.

Let us now consider the case, when some non-heat engine receives heat from outside at the T_0 ambient temperature. This is, in particular, the case of an endothermic reaction running in a fuel or galvanic cell. In this case equation (9.5.2) becomes:

$$W_i^e = M^*(h_1 - h_0) + Q_0, \qquad (6.6.3)$$

where $Q_0 = M^*T_0(s_0 - s_1)$ – amount of heat received from the environment.

As it follows from this expression, the heat flow, in this case, contribute to the fuel or galvanic element work. This fact has often been mentioned by the authors of electrochemical guidelines. However, it would be a mistake to suppose that the heat energy is here as well converted into ordered forms of energy. The fact is that in this case the heat flow from outside just compensates the system free energy consumption needed to cover the working medium bound energy $T_0(s_0 - s_1)$ increasing in course of the chemical transformations. The comprehension of this circumstance is significantly facilitated with division of the system energy U into the inergy E and anergy $\bar{U}$. According to energy balance (2.5.6) in a reversible process, whenever the system anergy remains unvaried, the useful work W^e done by the system is equal to the system ynergy decline:

$$W^e = -\Delta U = -(\Delta E + \Delta\bar{U}) = -- \Delta E\,. \qquad (6.6.4)$$

However, if there are some processes running in a system resulting in its anergy $\bar{U}$ increase (chemical or phase transformations, destructive and other dissipative processes associated with increasing entropy), the useful work decreases according to the anergy increase $\Delta\bar{U}$:

$$W^e = -\Delta E - \Delta\bar{U} \leq -- \Delta E. \qquad (6.6.5)$$

If at these conditions the anergy increase $\Delta\bar{U}$ is covered not due to the ynergy, but due to external anergy sources, e.g. by the heat exchange $Q_0 = \Delta\bar{U}$, the work done by the system will still be equal to the system ynergy decline as in the reversible run of the process:

$$W^e = -\Delta E - \Delta\bar{U} + Q_o = -\Delta E. \qquad (6.6.6)$$

However, the heat supplied to the system in this case is not converted into other forms of energy, but just replenishes the anergy increase. The efficiency of such a system must be naturally defined as the work W^e related to the entirely consumed energy $E_i' = A_r + Q_o$, but not to only the chemical reaction affinity $A_r = -\Delta E$, and therefore is always below unity. This means that no laws of thermodynamics are violated herein.

Thus the ban on using in heat engines the heat dissipated from the environment is once again caused by the arbitrary extrapolation of the thermodynamic laws beyond their applicability. However, the inadmissibility of such extrapolation at the present state of thermodynamics is far from being evident.

The in-depth comprehension of the processes running is somewhat facilitated from the positions of thermodynamics of irreversible processes (TIP) based on the concept of interaction between various flows and "entrainment" of one flow by other (in this case the heat flow entrained by the substance flow). However, such interaction is restricted in TIP to flows and forces of the same tensor order, so this theory can not elucidate the connection between the scalar chemical reactions and vector heat flows. The more advisable appears to be the consideration of these issues from the positions of thermokinetics. If from these positions, there is no wonder in the published information on the development, patenting and manufacturing of devices using the environmental heat to increase the useful work obtained in these devices (A. Serogodsky, 1992; S. Klimov,1992; G. Bujnov, 1992; G. Skornjakov, 1992; N. Zaev, 1992, and others). There are enough of facts evidencing the increased integrity of fuel, galvanic, electrolysis, etc. devices working on the absorption of heat from the environment. We can not but hope that thermokinetics will remove the suspicion about them on the part of official science and will promote searching the most successful engineering solutions in this field.

Chapter 7

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 thermokinetics. 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.

7.1. 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:

$$S = \Sigma_k N_k(\mathrm{c}_{\mathrm{v}k}\ln T + R_k \ln \upsilon_k + s_{ok}), \qquad (7.1.1)$$

where R_μ – universal gas constant; N_k – mole number of the k^{th} substance; c_{vk}, υ_k, s_{ok} – isochoric heat capacity, partial volume and entropic constant of a mole of the k^{th} 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.

It is significant that Gibbs did not at all consider expression (7.1.1) 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

$$S - [M_1R_1\ln(V/2) + M_2R_2\ln(V/2)] = R_{\mathrm{c}}\ln 2, \qquad (7.1.2)$$

where $R_{\mathrm{s}} = M_1R_1 + M_2R_2$ – 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 (18.1.1). In fact, (18.1.1) 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

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1) Here, unlike the original, 1 mole is adopted as a quantity unit of the k^{th} substance

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 regarding the character of their variation (M. Planck, 1925); (3) discrete variation 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 equalizing composition.

It is just a minor part of investigators (J. Van der Vaals, F. Konstamm, 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 paradox.

7.2. 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 impossible 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 convincing.

Classic thermodynamics dealing with only closed systems is known to have been interested in only the variation of entropy, but not its magnitude. This entropy variation in course of some process does not depend on whether a system is considered as a mixture of the k^{th} 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:

$$\Delta S = \Sigma_k N_k R_\mu \ln T/T_\text{o} - \Sigma_k N_k R_\mu \ln p/p_\text{o}, \qquad (7.2.1)$$

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

It follows from the identity of equations (7.2.1) 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:

$$pV = MRT;\ U = C_vT, \tag{7.2.2}$$

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 (10.1.1) was based on the analogy of the fundamental equation with Dalton law

$$p = \Sigma_k M_k R_\mu T/V \tag{7.2.3}$$

With regard to equation (7.1.1) 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 (7.1.1) 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:

$$\partial S_k(N_k)/\partial N_k = S_k(N_k)/N_k\,. \tag{7.2.4}$$

Expression (7.2.4) is compatible with (7.1.1) 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 (7.1.1):

$$\partial S_k(N_k)/\partial N_k = s_k(N_k) - R_\mu, \tag{7.2.5}$$

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 Ex systems at the mixing of gases. According to the Gibbs' mixing theory which does not involve any parameters characterizing differences between gases, the exergy loss ΔEx_{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:

$$\Delta Ex_{\text{см}} = T_{\text{о}} \Delta S_{\text{см}} . \tag{7.2.6}$$

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):

$$Ex_{\text{p}} = H - H_{\text{o}} - T_{\text{o}}(S - S_{\text{o}}) + R_{\text{c}} T_{\text{o}} \Sigma_k \ln p_k / p_{ok}, \tag{7.2.7}$$

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 i^{th} 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 k^{th} substances in the system p_k and the environment p_{ok}.

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

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.

7.3. 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 concentration 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 k^{th} substances among them (i.e. a mass transfer among them). In this case, because additional degrees of freedom appear (related to the k^{th} substances exchange), the exact differential of the system entropy becomes:

$$dS = (\partial S/\partial T)dT + (\partial S/\partial p)dp + \Sigma_k (\partial S/\partial N_k)dN_k \, . \qquad (7.3.1)$$

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 (7.1.1) via caloric state equation (7.2.2) the following forms may be found:

$$(\partial S/\partial T)_{V,N} = C_v/T\,;\ (\partial S/\partial P)_{T,N} = -MR_c/P. \qquad (7.3.2)$$

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 (6.5.1) should be applied, which gives:

$$(\partial S/\partial N_k)_{T,V} = s_k\,, \qquad (7.3.3)$$

where s_k – partial molar entropy of the k^{th} component, i.e. the value characterizing the entropy S rise in an open system when one mole of the k^{th} 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:

$$dS = (C_v/T)dT + (MR/V)dV + \Sigma_k\, s_k dN_k. \qquad (7.3.4)$$

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:

$$S = C_v \ln T + NR_\mu \ln \upsilon + \Sigma_k \textstyle\int s_k dN_k + S_o\,. \qquad (7.3.5)$$

This expression differs from (7.1.1) 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 (7.3.4) 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 (7.3.5). This value necessarily varies at the mixing in course of diffusion of the k^{th} 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 $\Delta S_{0\text{-}1} = \Sigma_k N_k R_\mu \ln T_1/T_o$. 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 $\Delta S_{2\text{-}3} = -\Delta S_{0\text{-}1}$. 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 $S_3 = S_2 + \Delta S_{2\text{-}3} = S_o + \Delta S_{mix}$. 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 (7.1.1) 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 thermokinetics 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.

7.4. 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 thermokinetics. Thermokinetics 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 system 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 k^{th} substances' distribution $\mathbf{Z}_{\text{k}}$. As any irreversible process, this may be maintained from outside, e.g. by feeding the k^{th} 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 $M = \Sigma_{\text{k}}M_k$ or the mole number in it $N = \Sigma_{\text{k}}N_k$. 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 k^{th} 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 6.1, 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:

$$S = \Sigma_k N_k s_k; \; V = \Sigma_k N_k \upsilon_k \, , \tag{7.4.1}$$

and considering (6.1.3) obtain:

$$\Delta S_{mix} = \Sigma_k N_k (s_k - s_{ko}); \; \Delta V_{mix} = \Sigma_k N_k (\upsilon_k - \upsilon_{ko}). \tag{7.4.2}$$

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

$$q_k^* = T(s_k - s_{ko}) \tag{7.4.3}$$

– 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 $\Sigma_k N_k(\upsilon_k - \upsilon_{ko})$ characterizes the bulk effects arising at the mixing of interacting components, while the value

$$w_k^* = p(\upsilon_k - \upsilon_{ko}) \tag{7.4.4}$$

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

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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 k^{th} substance in the absence of temperature gradient becomes possible just “a posteriori” (by experimental results)

Thus the thermal and the bulk effects q_k^* and w_k^* described by expressions (7.4.3) and (7.4.4) 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 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 reagents. 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

$$W^d = \Sigma_i \mathbf{F}_i \cdot d_u \mathbf{R}_j, \qquad (7.4.5)$$

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.

Chapter 8.

DENIAL OF THE THEORY OF "HEAT DEATH" OF THE UNIVERSE

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. In this chapter we are considering this issue from more general positions of thermokinetics and making an attempt to expose the sources of this mistake which has led to the concept of heat death of the Universe contradicting the today's vision of the world.

8.1. Reasons of Appearing Concept of "Heat Death" of the Universe

The authorship of the heat death theory belongs to R. Clausius, the founder of thermodynamics, who came to such a conclusion based on the law of entropy rise he himself formulated. The concept of entropy as itself was introduced by him due to a necessity to find the reversible heat exchange coordinate, i.e. a physical value necessarily varying at this process and remaining constant in its absence. Why shouldn't this value have kept a low profile as just one of the system energy independent arguments! However, R. Clausius noticed that, unlike other state coordinates (mass, volume, charge, momentum), entropy did not remain constant in isolated systems and spontaneously rose as such systems were approaching equilibrium. That unusual property of entropy as the only known then inconstant value restrained Clausius for some time from publishing the results of his investigation. However, the logic of the thermodynamics development and the intention to use that property of entropy to find the criteria of evolution and equilibrium for thermodynamic systems had such an outcome that Clausius not only raised the entropy rise law to the rank of the second law of thermodynamics, but also spread it over the entire Universe. Such an extrapolation of the entropy rise law 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 a disposition of Providence in the “Creation of the Universe” and to the inevitability of its “heat death”. To a good few of investigators such an extrapolation of the entropy rise law seemed extremely unconvincing yet in that time (J.M. Gelfer, 1979). However, despite the hot arguments over the issue, the status of the entropy rise law has not practically changed. In this connection it is of interest to clarify how the entropy has converted from an independent parameter of equilibrium system into the function of non-equilibrium state of the Universe as a whole.

One on these reasons, strange as it may appear, is the absence of other entropy-independent criteria of thermodynamic systems’ evolution. The finite-rate real processes are known to be a sequence of non-equilibrium states. The relaxation processes inevitable in this case cause spontaneous variations of the state parameters. That fact was first reflected in entropy balance equation (4.3.2) and became a ground to declare the entropy rise law. Now we are able to show that the similar principle may be as well set up regarding other state coordinates of a poly-variant system.

As shown in Chapter 9 the efficiency of any cyclic engine converting energy of whatever source demonstrates the same behavior as the heat engine. In this case the R. Clausius’ reasoning to substantiate the entropy rise law (Chapter 4) may be as well extended to non-heat engines. Let us consider an arbitrary cycle of a non-heat engine by substituting the coordinated T and S in Fig. 4.1 for Ψ_i and Θ_i. Following Clausius, let us divide this cycle with a series of vertical lines into a number of elementary reversible cycles similar to Carnot cycle. In each of these cycles the energy E_i' is supplied at a constant value of the potential ψ_i', while the same-kind energy E_i'' is removed at a constant value of the potential ψ_i''. Then according to (6.2.1) the elementary cycle efficiency will be defined by the relationship:

$$\eta_i = W_j / U_i' = 1 - \psi_i''/\psi_i'. \qquad (8.1.1)$$

Let us accept after Clausius that the efficiency η_i of any irreversible engine is less than that of a reversible one (at the same values of potentials characterizing the source and the receiver of the i^{th} kind energy – ψ_i' and ψ_i'', respectively). Then the sign of equality in relationship (8.1.1) may be substituted for the sign of inequality:

$$\eta_i \equiv 1 - đU_i''/đU_i' < 1 - \psi_i''/\psi_i' . \qquad (8.1.2)$$

Allowing for the signs $U_i' < 0$; $U_i'' > 0$, based on (8.1.2) gives $đU_i'/\psi_i' + đU_i''/\psi_i'' > 0$, i.e.

$$d\Theta_i > đU_i/\psi_i. \qquad (8.1.3)$$

Thus entropy is by no means the only parameter spontaneously varying due to irreversibility. This is the way the following parameters behave: the masses of the k^{th} substances M_k (due to phase transitions and chemical reactions), their momentum $M_k\mathbf{v}_k$ (due to relative motion dying out), the value V (at extension into void), the polarization vectors P and magnetization vector M (due to relaxation), etc. Therefore A.A. Guhman (1947) is right telling that entropy has become the evolution criterion on account of a number of historical reasons. A number of other mistakes hereafter described have as well contributed to this.

8.2. Discrimination between Thermodynamic and Statistical-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 3, 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 sys-

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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).

tem. The internal thermal energy $U_{\text{т}}$ 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 crushing, 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:

$$S = k_{\text{Б}} \ln \hat{W}, \tag{8.2.1}$$

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 (8.3.1), 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 $\hat{\mathrm{W}}$ 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 (8.3.1) 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 F

and the Gibbs *G* energies, which much more profoundly reflect the variation of a state than the bound energy TS. Besides, these, 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 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).

8.3. Correction of Entropy–Dissipation and Entropy–Irreversibility Relations

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 associated with the "path branching" is another kind of irreversibility (K. Denbigh, 1989). Since according to the TIP, when some non-static process is running, all available in the system thermodynamic forces of the same tensor order are overcome, then depending on these forces' nature (mechanical, electrical, chemical, surface, magnetic, etc.) the energy is converted into not only heat, but also other its forms. In this case even in the absence of the dissipation it is impossible to return to the process start-up by just reversing the sign of one of these processes – the reversal of the sign and value of all thermodynamic forces being overcome in the direct process will be needed. It is generally the same difficult as metastasis eradication in advanced cancer case. Because of this the polyvariant systems subjected to the action of many forces can develop irreversibly (i.e. in one direction) never returning to exactly initial state. This is how the Universe is developing according to the up-to-date conceptualization.

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.

8.4. Inconsistence of Entropy Rise Principle

That was not done, however. Furthermore, in the TIP the specific entropy was as well considered according to the local equilibrium hypothesis as a function of the same number of the specific thermostatic variables u, υ_k, c_k, т.е. $s = s(u, \upsilon_k, c_k)$. Meantime, the Universe as a system possesses the incomparably more degrees of freedom including that gravitational, radiant, chemical, intra-atomic, intra-nuclear, etc. So the under-determinacy of the Universe as a system is evident with all consequences ensuing. The correct proof of the entropy rise law should have been evidently rooted in the knowledge of the entropy as a function of all independent parameters of its state. However, such equations for the Universe in whole were unknown to Clausius and have remained so until the present. At these conditions the extrapolation of the conclusions Clausius made from the simplest thermo-mechanical systems to the whole Universe can not be estimated other than an evident violation of the methodological principles of thermodynamics. Later we will see that the entropy being substituted for more representative functions of state of non-equilibrium systems not only eliminates the conclusion of the inevitable heat death of the Universe, but also allows finding criteria more adequate to the character of the processes observed in it.

Furthermore, as shown in Chapter 6, the internal wells are in principle attributed to not only entropy, but also to many purely "thermostatic" variables (in particular, the masses M_k of the k^{th} substances, which can appear or disappear in chemical reactions, the volume V, which can spontaneously increase when a system expanding to an underpressure zone (and according to the special theory of relativity – at also relativistic acceleration of the system). They are also attributed to the parameters characterizing material structural defects, e.g. the number of dislocations, the size of crystal grains and nuclei of a new phase, etc., as well as to all relaxation process coordinates Z_i without exception. Therefore, from an up-to-date standpoint, Boltzmann did not have any reasons to consider the entropy proper as a state probability measure. In fact, according to (5.3.3) the entropy rises in only dissipative processes and, besides, in only those of them, where ordered forms of energy are converted into heat energy. In other words, the dissipation heat release and the associated entropy rise are just a part of the state variations associated with the energy dissipation and, more importantly, with irreversibility. This circumstance once again shows off the conclusion that the entropy rise can not serve as a measure of not only " any and all" irreversibility, but either the "dissipation at all".

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

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

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".

According to the above-mentioned it was the statistical-informational interpretation of entropy as antipode of "organization", "order", "complexity", etc. that made it a measure of "any and all" irreversibility. Therefore the question is quite natural what purely thermodynamic arguments substantiate the so sweeping generalizations of the entropy rise law. As we are now starting to guess, there are no and, in substance, can not be general proofs of this law. This is especially evident from the positions of thermokinetics, 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). In fact, any dissipative processes are irreversible. However, by no means any irreversible process is dissipative. In particular, mixing of isotopes or isomers of the same-kind atoms at the same temperature and pressure is an irreversible process. However, this process does not involve heat release and loss of capability to do work since the system of non-interacting gases having just two degrees of freedom yet before mixing was in complete (thermal and mechanical) equilibrium. For interacting gases, as shown in the previous chapter, the mixing process involves the "mixing heat" release and appearance of internal heat wells. Such wells appear in all processes associated with converting ordered forms of energy into anergy. This is what happens, e.g., at mixing of gases having different temperatures and thus – a certain inergy.

As for the reasoning based on the "matter-of-course" affirmation that the efficiency of any irreversible machine is less that the efficiency of a reversible one, it is invalid for even heat engines. Just imagine a heat engine, for which the heat source are tanks containing various isotopes, isomers or isobars of the same ideal gas at the same temperature. At their isothermal mixing the temperature of the heat source and subsequently the efficiency of the heat engine will not change, though the mixing process itself was irreversible in the system heat source–working medium–heat receiver. The efficiency will not change either at the isothermal throttling of the gas being the heat source, though this process is irreversible as well. These examples once again confirm that the entropy internal wells appear in only the cases when the dissipative work (against the dissipative forces) $W^D = W_R - W_{IR}$ involves releasing the dissipation heat Q^d. Should this conversion be absent, the entropy wells will not appear. However, the equality $W^d = Q^d$ can also be violated as it was in the said processes of metal cutting or material crushing. If so, the change of a part of inergy during dissipation to the strain, surface and other non-heat forms of energy may be revealed experimentally by, e.g., the difference between the isothermal dissolution heats of the initial and the strained materials2). There are also other processes, where some forms of the ordered energy are spontaneously converted into other similar forms at a negligible dissipation. The entropy rise does not reflect at all the nature of such processes. 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).

8.5. Inadmissibility of Entropy Rise Principle as Extrapolated to the Universe

The Boltzmanns' probabilistic interpretation of the second law of thermodynamic first looked like a lifebuoy among the attempts to impose an inevitable destiny on the Universe. According to the Boltzmann's interpretation of the second law of thermodynamics, the tendency of the Universe toward thermal equilibrium reflects just the most probable, though not at all unconditional direction of its evolution. There are large-scale fluctuations possible in various zones of the infinite Universe, i.e. spontaneous deviations from equilibrium involving the local decrease of entropy. In this case the entropy of the Universe rises just in the mean, while the world we are living in is a gigantic fluctuation.

However now, with experimental facts accumulated, such a concept of the Universe seems more and more metaphysical. It is noted on this account in one of the most solid study guides on thermodynamics (M.P. Vukalovich, I.I. Novikov, 1968), "In spite of the generally progressive character of the L. Boltzmann's ideas, it is nevertheless necessary to indicate a known metaphysical nature of his fluctuation hypothesis. The drawback of this hypothesis lies in the fact that the probability of such a gigantic fluctuation is too low to be realized. Its metaphysical nature can be seen from the following. According to this hypothesis the entire development of the Universe is re-

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2) This is the way, e.g., the difference between heat capacities of a strained and unstrained spring is revealed

duced to random deviations (fluctuations) from the state of thermodynamic equilibrium, where the Universe is staying. This is not so actually. The development of the Universe is a continuous complex process that could be instantiated by the formation of new stellar systems… In the widest sense the up-to-date picture of the world does not allow considering the development of the Universe as its transition to more and more probable states".

In this context a question arises about the propriety of extrapolation of whatever statements of thermodynamics to the systems which state equations or, at least, the degrees of freedom are unknown. In fact, thermodynamics gets knowledge of the properties of an object of investigation from the state and transfer equations taken from outside as uniqueness conditions of a kind. These equations reflect the relationship between the parameters of various degrees of freedom of a system under investigation. In the days of Clausius and Thomson, when the simplest thermo-mechanical systems, such as ideal or real gases, were considered, it was quite natural to adopt for an evolution criterion the entropy S as a quantitative measure of heat motion since the bound energy rise was the only consequence of approaching equilibrium in such systems. However, in poly-variant systems, such as the Universe, which, besides heat, possesses also other forms of energy (kinetic, gravitational, chemical, radiant, intra-atomic, intra-nuclear, etc.), the multivarious manifestation of irreversibility reduced just to the entropy rise looks, to say the least, fancy. Looking back one can not help being in a puzzle how the entropy has transformed from the argument of such a characteristic state function as system energy into a global function of state of the whole Universe. In fact, the energy in the thermo-mechanical systems the Clausius' theory referred to was considered as a function of two independent variables, viz. the coordinates of heat exchange and the cubic strain $U = U(S,V)$ processes. In this case the system entropy S as an inverse function takes the form $S = S(U,V)$ and for the isolated Universe (U,V = const) should remain unvaried. Hence, to substantiate the entropy rise from a formal mathematical standpoint, the entropy should have been considered as a function of larger number of variables, at least a part of which could vary spontaneously (had internal wells). Such are, in particular, the spatial heterogeneity parameters $\mathbf{Z}_i$.

According to the above-mentioned it was the statistical-informational interpretation of entropy as antipode of "organization", "order", "complexity", etc. that made it a measure of "any and all" irreversibility. Therefore the question is quite natural what purely thermodynamic arguments substantiate the so sweeping generalizations of the entropy rise law. As we are now starting to guess, there are no and, in substance, can not be general proofs of this law. This is especially evident from the positions of thermokinetics, 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). In fact, any dissipative processes are irreversible. However, by no means any irreversible process is dissipative. In particular, mixing of isotopes or isomers of the same-kind atoms at the same temperature and pressure is an irreversible process. However, this process does not involve heat release and loss of capability to do work since the system of non-interacting gases having just two degrees of freedom yet before mixing was in complete (thermal and mechanical) equilibrium. For interacting gases, as shown in the previous chapter, the mixing process involves the "mixing heat" release and appearance of internal heat wells. Such wells appear in all processes associated with converting ordered forms of energy into anergy. This is what happens, e.g., at mixing of gases having different temperatures and thus – a certain inergy.

As for the reasoning based on the "matter-of-course" affirmation that the efficiency of any irreversible machine is less that the efficiency of a reversible one, it is invalid for even heat engines. Just imagine a heat engine, for which the heat source are tanks containing various isotopes, isomers or isobars of the same ideal gas at the same temperature. At their isothermal mixing the temperature of the heat source and subsequently the efficiency of the heat engine will not change, though the mixing process itself was irreversible in the system heat source–working medium–heat receiver. The efficiency will not change either at the isothermal throttling of the gas being the heat source, though this process is irreversible as well. These examples once again confirm that the entropy internal wells appear in only the cases when the dissipative work (against the dissipative forces) $\mathrm{W}^{\mathrm{D}} = \mathrm{W}_{\mathrm{R}} - \mathrm{W}_{\mathrm{IR}}$ involves releasing the dissipation heat Q^{d}. Should this conversion be absent, the entropy wells will not appear. However, the equality $W^{\mathrm{d}} = Q^{\mathrm{d}}$ can also be violated as it was in the said processes of metal cutting or material crushing. If so, the change of a part of inergy during dissipation to the strain, surface and other non-heat forms of energy may be revealed experimentally by, e.g., the difference between the isothermal dissolution heats of the initial and the strained materials2). There are also other processes, where some forms of the ordered energy are spontaneously converted into other similar forms at a negligible dissipation. The entropy rise does not reflect at all the nature of such processes. Therefore the remark is absolutely true that the

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2) This is the way, e.g., the difference between heat capacities of a strained and unstrained spring is revealed

question regarding the physical grounds of the monotonic entropy rise remains … still open" (L. Landau, E. Livshits, 1973).

8.6. Processes in the Universe as Reciprocal Antipodes

According to the deductive methodology (from the general to the special) the Universe should be construed as an *entire set of interacting (relatively moving) bodies and particles*. Such a system is by definition isolated and closed, i.e. none of external forces act on it, and all processes are therein spontaneous. Strictly speaking, these are systems of such a kind the laws of conservation of energy, mass, charge, momentum and angular momentum are stated to apply to in the form excluding exchange between these systems and the environment. All forces acting in a closed system are internal (having not a resultant) and, due to equality between action and counteraction, appear and disappear in pairs only. Let us now introduce, by analogy with gas pressure and for convenience, the specific internal force of interaction between the body masses composing the Universe $\mathbf{f}$ (N/m^2), i.e. the force per unit closed surface area f (m^2). Then the resultant $\mathbf{F}$ of these forces will be defined as $\mathbf{F} = \int \mathbf{f} \cdot d\mathbf{f}$, where $d\mathbf{f}$ – vector element of system closed surface. For a closed system by definition this resultant $\mathbf{F} = 0$, therefore according to Gauss theorem:

$$\mathbf{F} = \int \mathbf{f} \cdot \mathbf{n}\, df = \int \mathrm{div}\mathbf{f}\, dV = 0. \qquad (8.6.1)$$

From (8.6.1) the resultant being equal to zero at $\mathbf{f} \neq 0$ is possible in two cases: (1) divergence of the force $\mathbf{f}$ is equal to zero everywhere (no gravitation) and (2) divergence of the force $\mathbf{f}$ has opposite sign for various bulk elements of a system under consideration. Let us assume, for example, $\mathrm{div}\mathbf{f} < 0$ in one of the bulk elements. Due to equality between action and counteraction this means that any couple of forces acting on the bulk element is directed toward each other causing its compression (approaching particles). This is what is interpreted as the attraction between particles. Then according to (8.6.2), in another domain of the Universe, $\mathrm{div}\mathbf{f} > 0$, i.e. the forces predominate, which cause particle-to-particle distance to grow. This evidently does not mean that the gravitational forces are replaced in such an element by the repulsion forces (anti-gravitation). It is just the sign of the stress caused by particle-to-particle gravitational interaction forces that has changed, i.e. the compression stress has been replaced by the tensile stress in this domain of the Universe. Thus processes having opposite directivity are inevitable in the spatially heterogeneous Universe. In other words, the Universe is *unstable* in terms of internal processes continuously running there and leading to mass concentration in certain domains of the Universe, stellar cluster formation in these domains, accretion, collapse, thermonuclear reactions initiated, "supernovas" produced, explosion followed by dissipation of the matter and its accumulation in other domains of the Universe with the same revolution of the events recurring therein. Recognition of this *dichotomy* gives a new evolution idea to the Universe principally differing from the Universe models accepted to date.

The extensive and intensive parameters of spatial heterogeneity introduced in Chapter 1,2 and pertaining to the Universe as the moments of distribution of all its inherent extensive properties $\mathbf{Z}_i$ and associated forces $\mathbf{X}_i$ are of fundamental importance to comprehend the peculiarities the evolution of the Universe features. These introduced made it possible to distinguish within the internal energy of a nonequilibrium system an ordered (convertible) part – the system inergy $E = \Sigma_i \mathbf{X}_i \cdot \mathbf{Z}_i$. This component generalizes the notion of Gibbs and Helmholtz free energy to open and spatially heterogeneous media. The ordered energy is expressed here directly in terms of the spatial heterogeneity parameters, which allows its finding for not only a system in whole, but also separately for each form of energy and degree of freedom pertaining to the system. This provides investigators with rather "physic", flexible, non-entropy criteria of the Universe evolution, which are much more informative than the entropy. Unlike the entropy capable to reflect just the approach of the Universe as a whole to equilibrium, the ordered energy can be found for each of the Universe-inherent degrees of freedom or space domain *dV*, which makes it possible to reflect both the approach of this domain or degree of freedom to equilibrium

$$dE_i = -\mathbf{X}_i \cdot \mathrm{d}\mathbf{Z}_i < 0, \tag{8.6.2}$$

and their moving away from equilibrium

$$dE_i = -\mathbf{X}_i \cdot d\mathbf{Z}_i > 0 . \tag{8.6.3}$$

The availability of such criteria immediately reveals the naturally existing tendency to state ordering, which manifests itself in the fact that spontaneous ordering processes in some domains of a nonequilibrium polyvariant system at any hierarchic level of the Universe run due to work done on them from other its domains or degrees of freedom, as well as due to decrease of their ordered energy. Such processes running in the mutually opposite directions are termed as *coupled* in nonequilibrium thermodynamics. As already noted, such anti-dissipative processes in the Universe involve redistribution of mass over its volume (including accretion processes), which results in collapse of associated cosmic objects, thermonuclear reactions initiated therein, their temperature rise, "supernova" outburst and explosion, stellar material scattering and subsequent "recycling" of the events in other domains of the Universe. Neither of the evolution criteria based on the entropy rise principle can predict the irreversible (one-sided) processes of such a kind existing, since the entropy or its "deficiency" (deviation from maximum) is just a reflection of how far a system in whole stands from equilibrium.

Such an approach makes it possible to state there are anti-relaxation processes running in the Universe (in the direction away from equilibrium) along with relaxation processes, whereupon the Universe develops omitting the equilibrium state. The direction of the processes running in separate domains of the Universe is determined by the resultant of all internal forces acting there, each of the component forces being defined as a derivative of the ordered energy of a particular kind with respect to the adequate moment of distribution. This means that the relationship between the forces of different kinds with the resultant of the same value may be quite different, which is what predetermines the process path in the space of the same variables that define the state of the system. This circumstance that K. Denbigh called the "path branching" is caused by many factors including the process sequence and the rate of each particular process and its reaction force. Processes of such a kind, even if dissipativeless, are irreversible at least because the sign reversal for any of the acting forces provokes the process to run along now another path. Therefore with this force reversed the inverse process runs through other states, while the system does not return to its initial state. This is what we mean when mention the process irreversibility in any part of the Universe.

For this reason the investigators' striving for using the entropic criteria of evolution in analysis of self-organization processes is a certainly good-for-nothing attempt. It is difficult to find a parameter to estimate the system order degree, which would be so much lame as entropy. This becomes even more evident when comparing the entropic criteria with the ordered energy (inergy) E as a measure of order of the system as a whole and each of its degrees of freedom separately E_i. These are functions of the parameters Z_r and $\mathbf{Z}_i$ not depending on the entropy S, which makes them a new and an extremely flexible tool of the thermokinetic analysis. First of all, it is worth noticing their simple and clear physical meaning as values characterizing the capability of a system to do useful (ordered) work (internal and external, respectively). It is extremely significant in this respect that the inergy of any degree of freedom E_i can be substantially found for a current state of a non-equilibrium system by known fields of temperatures, pressures, concentrations, etc, which significantly facilitates the prediction of their behavior in various processes without whatever calculations.

These criteria allow the same easy formulation of the process spontaneity criteria. According to the axiom of equilibrium self-non-disturbance the processes of system deviation from equilibrium can not be spontaneous. This means that *any spontaneous process is always directed toward establishing equilibrium of a particular kind*. This evident statement allows distinguishing natural processes from the "induced" (forced) ones. Such are, in particular, the so-called "coupled" chemical reactions, when some of them running toward equilibrium engender reactions of the opposite nature. This is quite significant in order to perceive the reasons of oscillation process generation and the character of state cyclic variations for systems under investigation including the "circulation" of substance and energy in nature (E. Lightfoot, 1977).

An unconditional advantage of inergy over entropy consists also in the utter determinacy of inergy magnitude, whereas only entropy variations when approaching equilibrium can be substantially found. Knowing the inergy magnitude allows introducing a specific criterion of local degree of order for the system as the relation between its inergy E and energy U:

$$\eta_\varepsilon \equiv E/U \tag{8.6.4}$$

Thus the inergy expressed exclusively in terms of the non-equilibrium parameters provides investigators with a very convenient, clear and universal criterion of evolution, equilibrium and stability of poly-variant systems, which leaves the entropy potentialities far behind.

It is significant that criteria (8.6.2)…(8.6.3) do not impose a line of behavior on the system since the sign of the dE_i variation is defined in thermokinetics by exclusively experimental method as one of the system properties the uniqueness conditions of a problem are based on. In particular, this criteria allow for the system development omitting equilibrium. In particular, thermokinetics well allows the development of the Universe with non-periodic continuous-wave mode of its particular zones, which is quite natural since the reaction forces (responses) from other zones lag given the infinity of the Universe.

The absolute definition of magnitude of inergy is its unconditional advantage over entropy which can be substantially defined as only its variations when approaching equilibrium. The availability of such criteria cardinally changes the results of such analysis. The application of entropy as a tool to analyze the evolution and self-organization problems can be now explained by solely investigators' ignorance or by their reluctance to bring thermodynamics to conformity with the scope of the problems to be solved.

The consideration initiated here brings us to comprehension that it is presently sensible to mention the evolution of not the Universe as a whole, but rather of its particular domain, for which observational astronomy allows to formulate uniqueness conditions. Only then it becomes clear what processes predominate in this particular part of the Universe – whether energy degradation ($\Sigma_i dE_i < 0$) or energy concentration ($\Sigma_j dE_j > 0$) – and what processes of energy transmutation cause a character of energy evolution. No theory can "dictate" a particular evolution scenario to the Universe. Theory just confirms that the isolated Universe develops in whole omitting the equilibrium state.

Chapter 9

NEGATIVE ABSOLUTE TEMPERATURE CONCEPT INVALIDITY

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.

9.1. Negative Absolute Temperature Notion Origin

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

$$T \equiv (\partial U/\partial S)_V \,, \tag{9.1.1}$$

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

$$n_i = n_0 \exp(-\beta\varepsilon_i) \qquad (9.1.2)$$

is related with the absolute temperature T by a simple relationship $\beta = 1/k_bT$, 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 i^{th} energy level ε_i as

$$n_i/n_0 = \exp[(\varepsilon_0 - \varepsilon_i)/k_bT]. \qquad (9.1.3)$$

If $T > 0$, then the population of higher energy levels according to (9.1.3) 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 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).

9.2. "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 absolute zero. The thermal efficiency of the reverse Carnot engine will then have the form:

$$\eta_t^{K} = 1 - Q_c/Q_h = 1 - T_c/T_h\,. \tag{9.2.1}$$

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 (9.1.4) 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 thermokinetics. 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 (9.1.1). In fact, according to (9.1.3) 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 (9.1.1) 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) pulse. 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 excludes 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 (7Li and 19F) 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:

$$T = (\Sigma_i C_i / T_i)/\Sigma_i C_i \,, \tag{9.2.2}$$

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 (9.2.2), 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 (9.2.2) 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).

9.3. Non-Thermal Nature of Spin-Spin Interaction

As already noted above, the same experiments considered from the positions of thermokinetics 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 = $E(\boldsymbol{\varphi}_i)$, 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 $E = E(\boldsymbol{\varphi}_i)$ has been hitherto studied with insufficient 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 thermokinetics 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 thermokinetics 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.

9.4. Description of Spin Systems from the Positions of Thermokinetics

Nuclear particles, when rotating, are known to undergo precession, i.e. a motion when the axes of their rotation make a spatially oriented angle $\boldsymbol{\varphi}_\mathrm{s}$ with the external field vector **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 $\mathbf{J}_\mathrm{s}$, but also on its spatial orientation (angle $\boldsymbol{\varphi}_\mathrm{s}$). Depending on this angle, the spin projection $\mathbf{I}_\mathrm{s}$ of the i^th elementary particles on a chosen spatial direction (e.g. on the external magnetic field **H** direction) varies from $-\mathbf{I}_s$ до $+\mathbf{I}_\mathrm{s}$ (which corresponds to $\varphi_\mathrm{s}= 180^0$ and $\varphi_\mathrm{s}= 0^0$). Hence the total angular momentum $\mathbf{J}_\mathrm{s}$ is related to the spin $\mathbf{I}_\mathrm{s}$ thru the relationship:

$$\mathbf{L}_\mathrm{c} = \mathbf{\Sigma}_i\, h\mathbf{I}_\mathrm{c} \cos \boldsymbol{\varphi}_c\,, \qquad (9.4.1\ )$$

where h – Planck constant.

Along with this, nuclei, atoms and molecules of condensed substances are known to possess some magnetic moment $\mathbf{Z}_м$ 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 $\mathbf{Z}_{\text{м}}$, but on also the relative orientation of spins (angle $\boldsymbol{\varphi}_{\text{s}}$). The parameters S, $\mathbf{Z}_{\text{м}}$ and $\boldsymbol{\varphi}_{\text{s}}$ are in principle independent so that the energy E of condensed substances as the function of their state looks like $U = U(S, \mathbf{Z}_{\text{м}}, \boldsymbol{\varphi}_{\text{s}})$, while its exact differential is expressed by the relationship:

$$dU \equiv TdS - \mathbf{H}d\mathbf{Z}_{\text{м}} - \mathbf{M}_c \cdot d\boldsymbol{\varphi}_c \,, \tag{9.4.2}$$

where $T \equiv (\partial U/\partial S)$ – absolute temperature of the system; $\mathbf{H} \equiv (\partial U/\partial \mathbf{Z}_{\text{м}})$ – external magnetic field intensity; $\mathbf{M}_{\text{s}} \equiv (\partial U/\partial \mathbf{J})$ – orientation moment. In this expression the term $\mathbf{M}_{\text{s}} \cdot \mathrm{d}\boldsymbol{\varphi}_{\text{s}}$ 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:

$$(\partial \mathbf{Z}_{\text{м}}/\partial \boldsymbol{\varphi}_c)_{\mathbf{H}} = (\partial \mathbf{Z}_{\text{м}}/\partial \mathbf{H})_{\boldsymbol{\varphi}}. \tag{9.4.3}$$

According to this relationship the angle of orientation polarization $\boldsymbol{\varphi}_{\text{s}}$ of a nuclear spin system varies under the influence of the external magnetic field **H** inasmuch as the system magnetization $\mathbf{Z}_{\text{м}}$ – due to the spin system reorientation (angular momentum $\mathbf{J}_{\text{s}}$ variation). However, the magnetic field **H** being constant, the $\mathbf{Z}_{\text{м}}$ 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}:

$$\mathbf{Z}_{\text{я}} = \gamma \mathbf{L}_{\text{c}} \,, \tag{9.4.4}$$

Then (9.4.2) may be substituted for:

$$(\partial \boldsymbol{\varphi}_c/\partial \mathbf{H})_{\mathbf{L}} = \gamma_c \,. \tag{9.4.5}$$

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 (9.4.3) 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 thermokinetics eliminates the paralogism of negative absolute temperatures confirming once again the inviolability of the laws of thermodynamics.

Chapter 10

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 thermokinetics. This chapter is dedicated to the situation arisen, which will be analyzed from the positions of thermokinetics.

10.1. 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:

$$Q' = Q\gamma \; ; \; T' = T\gamma \, , \tag{10.1.1}$$

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

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 $W_w' - W_w'' = Q'_h(1/\gamma - 1)$. Subtracting this work from the work W_c' gives:

$$W_\text{c} = Q_\text{г}(1 - T_\text{х}/T_\text{г}) - Q_\text{г}(\gamma - 1/\gamma). \qquad (10.1.2)$$

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

$$Q' = Q/\gamma\ ;\ \ T' = T/\gamma\ , \qquad (10.1.3)$$

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:

$$\mathbf{F}_w = d(M\mathbf{w}_m/\gamma)/dt, \qquad (10.1.4)$$

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

$$\mathbf{F}_w = Md(\mathbf{w}_m/\gamma)/dt\ . \qquad (10.1.5)$$

The distinction between those two are that expression (10.1.4) 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 (10.1.4) and (10.1.5) 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 (10.1.1) or (10.1.6). 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.

10.2. 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 expanding 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:

$$Q'_{\text{г}}/T_{\text{г}}' = Q_{\text{г}}/T_{\text{г}} = Q_{\text{х}}/T_{\text{х}}\,. \qquad (10.2.1)$$

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

$$W_{\text{ц}}' = Q'_{\text{г}} - Q_{\text{х}} = Q_{\text{г}}(1 - T_{\text{х}}/T_{\text{г}}') = Q_{\text{г}}(\gamma - T_{\text{х}}/T_{\text{г}}). \qquad (10.2.2)$$

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

$$\eta_t^{\text{К}} \equiv W_{\text{ц}}'/Q'_{\text{г}} = 1 - T_{\text{х}}/T_{\text{г}}\gamma\,. \qquad (10.2.3)$$

Thus the Planck's transformations did not allow for invariance of the Carnot cycle efficiency $\eta_{\text{t}}^{\text{C}}$ 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 (see 10.2.3) 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:

$$\eta_t^{\text{К}}{}_{(\text{Отт})} = 1 - T_{\text{х}}\gamma/T_{\text{г}}\,. \qquad (10.2.4)$$

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 (1) 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 thermokinetics.

10.3. 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 6.6.4) receiving energy from several sources of various nature:

$$\eta_i = W_j/\Delta U_i' = 1 - \Psi_i''/\Psi_i'.$$

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:

$$W_w = \Delta E^{\kappa} = \Delta M(c^2/\gamma_h - c^2/\gamma_c), \qquad (10.3.1)$$

where $\gamma_c = (1 - v_c^2/c^2)^{½}$; v_c – relative velocity of heat sink.

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

$$\eta_{(t+w)} = (W_t' + W_w)/(Q'_h + E^{\kappa}) = \eta_t\,\gamma_h + \eta_w(1 - \gamma\,\gamma_h), \qquad (10.3.2)$$

where

$$\eta_t = W_{\Gamma}'/Q'_h;\ \eta_w = W_w/E^{\kappa} = 1 - \gamma_h/\gamma_c \qquad (10.3.3)$$

– 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.

10.4. Inapplicability of Relativity to Absolute Values

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 self-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 $U(M)$:

$$U(M + \Delta M) = U(M) + Mc^2(1/\gamma - 1) = U/\gamma \,. \qquad (10.4.1)$$

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 self-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 self-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 self-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 thermokinetics. 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:

$$\gamma = 4m/(M + 2m). \tag{10.4.2}$$

According to (10.4.2) 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 (10.4.1) in the invariance of thermal efficiency of Carnot cycle.

However, thermokinetics 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, which position can be changed by no means according to the law of momentum conservation. While measuring such a velocity is problematic, the fact of its availability as itself is significant.

Being a deductive discipline, thermokinetics 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). Therefore the Poincaré-Lorentz-Einstein relativity principle requiring the invariance of physical laws stated relative to any inertial reference system is evidently inapplicable. In this respect thermodynamics may be considered as an “absoluteness theory”. In thermodynamics such reference systems are primary, wherein the laws of physical phenomena look especially simple. Such a standpoint evidently contradicts STR.

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 of thermokinetics, 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 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 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.

Part 4

FURTHER GENERALIZING OF HEAT ENGINE THEORY

Chapter 11

THEORY OF SIMILARITY OF ENERGY CONVERSION PROCESSES

Classic thermodynamics, having time excluded from its equations, did not considered the processes of energy and its carriers transfer. Therefore the issue regarding unity of energy transfer and conversion processes could not arise in its depths. N. Umov was the first (1873) who paid attention to that relation and stated the energy conservation law (2.3.6) for mechanical processes rather as a consequence of energy transfer across the system borders than as a result of energy disappearing in some points of space and appearing in others. It remained unanswered, however, what was the "transfer substrate" in that case – either the material energy carriers attributed to the extensive values Θ_i category or the intensive values ψ_i as analogs of mechanical stresses. Thermokinetics gives an answer to this question. According to (2.3.10) the flux $\mathbf{J}_{ui}$ of any i^{th} form of energy is expresses as the product of the intensive measure of motion – the generalized potential ψ_i – and the energy carrier flux $\mathbf{J}_i$ that is defined, in its turn, as the product of the extensive measure of motion Θ_i of this particular kind being transferred and the velocity $\mathbf{v}_i$ of its transfer in space. This flux density $\mathbf{j}_i$ is accordingly expressed as the product of the density $\rho_i = \rho\Theta_i$ of this extensive value and its transfer velocity $\mathbf{v}_i$. The transfer concepts extraneous to classic thermodynamics find thereby their realization in thermokinetics

Using the thermokinetic body of mathematics applicable for the investigation of processes with any irreversibility degree allows posing the issue of establishing general behavior of non-static energy conversion processes and thus enabling a synthesis of the theory of irreversible processes (TIP) with engineering thermodynamics dealing with the energy conversion process in heat engines.

This chapter highlights the new results in the theory of heat and non-heat, cyclic and non-cyclic machines, direct action machines and heat pumps obtained when applying the thermokinetic methods to them. One more step will thereby be done toward the creation of the unified theory of real processes.

11.1. Unity of energy Transfer and Conversion Processes

Classic thermodynamics, having time excluded from its equations, did not considered the processes of energy and its carriers transfer. Therefore the issue regarding unity of energy transfer and conversion processes could not arise in its depths. N. Umov was the first (1873) who paid attention to that relation and stated the energy conservation law (2.3.6) for mechanical processes rather as a consequence of energy transfer across the system borders than as a result of energy disappearing in some points of space and appearing in others. It remained unanswered, however, what was the "transfer substrate" in that case – either the material energy carriers attributed to the extensive values Θ_i category or the intensive values ψ_i as analogs of mechanical stresses. Thermokinetics gives an answer to this question. According to (2.3.10) the flux $\mathbf{J}_{ui}$ of any i^{th} form of energy is expresses as the product of the intensive measure of motion – the generalized potential ψ_i – and the energy carrier flux $\mathbf{J}_i$ that is defined, in its turn, as the product of the extensive measure of motion Θ_i of this particular kind being transferred and the velocity $\mathbf{v}_i$ of its transfer in space. This flux density $\mathbf{j}_i$ is accordingly expressed as the product of the density $\rho_i = \rho\Theta_i$ of this extensive value and its transfer velocity $\mathbf{v}_i$. The transfer concepts extraneous to classic thermodynamics find thereby their realization in thermokinetics.

Furthermore, thermokinetics allows easily distinguishing between the energy *transfer* processes (within the same form) and the energy *conversion* processes (from some form into another). With this purpose in mind let us consider a system with an arbitrary volume of V wherein a steady process of converting the i^{th} energy form into the j^{th} one is being realized. As shown in Chapter 2, this process is described by the second sum in the equation of energy conversion in the form (2.4.7), which terms characterize the capacity of energy conversion processes in the system.

The terms of this sum may be endued with a more conventional form if taking into consideration that the redistribution processes correspond to the expansion of $\nabla\cdot(\psi_i\mathbf{j}_i^{\mathrm{e}})$ into the (2.4.6) given that $\nabla\cdot\mathbf{j}_i^{\mathrm{e}} = 0$. For the system as a whole this condition becomes $\int\nabla\cdot\mathbf{j}_i^{\mathrm{e}}\, dV = 0$. Changing in this expression from the space integral to the integral $\int\mathbf{j}_i^{\mathrm{e}}\cdot\boldsymbol{n}\, df = 0$ taken through the closed surface f of the system gives that at $\mathbf{j}_i^{\mathrm{e}} \neq 0$ the said condition indicates the parts f' and f'' existing on this surface with the opposite sign of the $\mathbf{j}_i^{\mathrm{e}}\cdot\mathbf{n}$

product, i.e. the flows $\mathbf{j}_i'$ and $\mathbf{j}_i''$ existing as entering the system and leaving it, respectively. In this case

$$\int \mathbf{j}_i \cdot \mathbf{n}\, df = \int \mathbf{j}_i' \cdot \mathbf{n}\, df' + \int \mathbf{j}_i'' \cdot \mathbf{n}\, df'' = J_i'' - J_i' = 0, \tag{11.1.1}$$

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

Thus in balance equation (2.4.3) the external component of the flow $\mathbf{J}_i^{\mathrm{e}}$ caused by the useful external work W^{e} done may be distinguished from the relaxation component $\mathbf{J}_i^r$ by the conservation of the energy carrier flow rates J_i' and J_i'' at the system input and output. Representing in (2.3.7) the bulk element dV covered by the flow $\mathbf{j}_i^{\mathrm{e}}$ as a product of its cross section vector element $d\mathbf{f}$ normal to the flow and the normal element $d\mathbf{n}$ ($dV = d\mathbf{f} \cdot d\mathbf{n}$) and also considering that in a steady flow $(d\mathbf{n} \cdot \nabla)\psi_i = d\psi_i$ one may derive instead of the addend in (2.3.7):

$$N_i = \int \left(\int \mathbf{j}_i^{\mathrm{e}} \cdot d\mathbf{f} \right) d\psi_i = -\int J_i^{\mathrm{e}} d\psi_i = J_i^{\mathrm{e}} (\psi_i' - \psi_i''), \tag{11.1.2}$$

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

Thus the useful component is associated with the “transit” flow of energy carrier J_i^e which crosses the system with its value invariable. This statement may be instantiated by an electric machine where the input current is known to be equal to the output one. This is equally evident for a cyclic heat engine, too (Fig. 3-1), since in any cycle the entropy rise with the heat supply $\Delta S_{1\text{-}2}$ is numerically equal to the entropy decline $\Delta S_{2\text{-}1}$ with the heat rejected to heat sink. Therefore, at steady conditions the entropy flow rates $J_s^e = \Delta S/\Delta t$ at the system input and output are as well equal. This is the circumstance that was foundational for S. Carnot to compare heat engine with a mill-wheel (hydraulic machine).

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

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

Expression (13.1.2) is valid for both the i^{th} (being converted) and the j^{th} (having been converted) forms of energy. This means that any energy converting device (both cyclic and non-cyclic) is a system “transfused” with the energy-carrier flows of both “being-converted” $\mathbf{J}_i$ and “having-been-converted” J_j forms of energy. Such a “two-flow” system in electrical engineering is represented as a “four-terminal” network in electrical engineering and radio-engineering, i.e. a device with two pairs of input and output terminals. For clearness, an electrical “equivalent circuit” to an energy converting device is shown in Fig. 11.1.

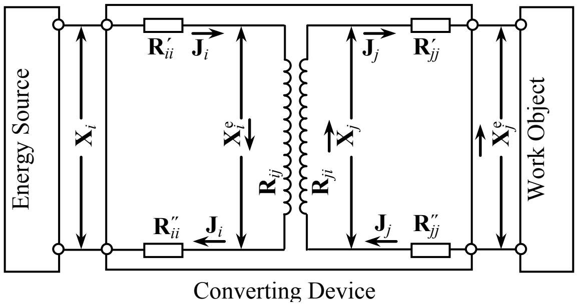


Fig.11.1. Electrical Equivalent Circuit to energy Converting Device

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

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

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

11.2. Universal Index of energy Converters’ Perfection

The necessity to have both wells and sinks of entropy, charge, substance, momentum, etc. ensuing from (13.1.2) once again emphasizes the flexibility of the law of excluded perpetual motion of the second kind. This statement results in a possibility for each of the energy converting devices to be estimated by the process power N_i related to the energy flow at the inlet to the energy converter J_e':

$$\eta_i = N_i / J_e' = N_i = 1 - \bar{\psi}''_i / \bar{\psi}'_i, \qquad (11.2.1)$$

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

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

Let us now show that expression (11.2.1) is valid for cyclic heat engines, too. To do so, let us interrelate the so-called “mean-thermodynamic” temperatures $\overline{T}_1$ and $\overline{T}_2$ in the heat absorption and rejection processes with the mean-integral temperatures T_s' and T_s'' of entropy flows at the device inlet and outlet. If ΔS_1 and ΔS_2 characterize the variations of the working medium entropy with the heats absorption and rejection Q_1 and Q_2 in some cycle, while Δt_1 and Δt_2 – duration of these processes, then the total flows of heat J_q' and J_q'' and entropy J_s' and J_s'' will be defined as:

$$J_q' = Q_1/\Delta t_1 \,;\, J_q'' = Q_2/\Delta t_2 \,; \tag{11.2.2}$$

$$J_s' = \Delta S_1/\Delta t_1 \,;\, J_s'' = \Delta S_2/\Delta t_2 \,. \tag{11.2.3}$$

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

$$\overline{T}_1 = Q_1/\Delta S_1 = J_q'/J_s' = T_s' \,, \tag{11.2.4}$$

$$\overline{T}_2 = Q_2/\Delta S_2 = J_q''/J_s'' = T_s''. \tag{11.2.5}$$

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

$$\eta_t = 1 - Q_2 / Q_1 = 1 - T_2/T_1 = 1 - \overline{T}_s''/\overline{T}_s' \,. \tag{11.2.6}$$

Then

$$J_s' = J_q'/T_s' = J_s'' = J_q''/ T_s'' \,. \tag{11.2.7}$$

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

$$N^e = J_q'\eta_t = J_s'\,(T_s' - T_s'') = J_s'\Delta T_s, \qquad (11.2.8)$$

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

The unified expression of absolute efficiencies for heat and non-heat, cyclic and non-cyclic engines (see 11.2.1) shows that this value depends on neither a kind of the energy being converted and design of the energy converting device, nor on its working medium nature or parameters. Therefore the value η_i , as well as η_t, strictly speaking should not at all be termed as "engine efficiency". This value is defined by exclusively the parameters of the "hot" and "cold" energy well on the border with the working medium, i.e. by the energy flow parameters, but not the properties of the engine as itself. In other words, the "absolute efficiencies", including the "thermal", "internal", "effective", "electrical", "enthalpy", etc. efficiencies widely used in analysis of heat power units characterize rather the capabilities provided by nature due to its intrinsic spatial heterogeneity in dispensing of whatever intensive property. These efficiencies characterize just the maximal "convertibility degree" of a particular energy form, which is attained in the same machine with the quasi-static nature of the processes involved therein (when all the processes are "reversible"). According to the Carnot theorem this efficiency does not depend anymore on the working medium properties within the energy converting device, i.e. relates to some abstract (idealized) machine naturally not occurring. Since all reversible processes are infinitely slow running, the power of such a machine is infinitesimal. Therefore in thermokine- tics dealing with real processes and machines we will be avoiding to apply the term "efficiency" to the value η_i terming it rather "energy convertibility degree".

The so-called "relative" efficiencies have other meaning. In classic thermodynamics this notion is introduced in order to estimate the perfection of particular processes in heat power engines, e.g. the working medium expansion processes. Such efficiencies mean the work W_i actually done in the process related to its theoretically possible value W_i^t (A. Andrushchenko, 1985). These are the efficiencies (relative) all other disciplines operate except thermodynamics. For non-cyclic machines doing one kind of the useful work these efficiencies actually characterize the perfection degree of a machine (i.e. the losses therein). The fact that thermodynamics operates absolute efficiencies, whereas the other disciplines operate relative ones, has caused confusion time after time. Quite often lamentations have been raised for a low efficiency of heat power stations and up-to-60%-of-fuel heat "wasted" to the environment, whereas the efficiency of fuel cells, electric and many other machines reaches 90% and above. But for all that it has never occurred to the "complainants" that only several percents of the Q_2 heat given away in excess of a certain minimum of Q_{2t} can be referred to the so-called "wasted heat loss" since the heat Q_{2t} rejected according to (13.1.3) is not a loss, but the *condition necessary to provide the energy conversion process as itself.*

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

$$\eta_N = N_j / N_i = X_j J_j^{\mathrm{e}} / X_i J_i^{\mathrm{e}} \leq 1 \ . \qquad (11.2.9)$$

This expression is quite close by implication to the notion of relative internal efficiency of heat engines in classic thermodynamics and goes over into it after multiplication of the numerator and denominator in (11.2.1) by an arbitrary time span Δt. In this case the (11.2.1) numerator characterizes the useful work actually done by the machine $W_i = X_j J_j^e \Delta t$, while the denominator – its theoretically possible value $W_i^t = X_i J_i^{\mathrm{e}} \Delta t$. We will be terming the (11.2.1) ratio a "power" efficiency of the energy converting device. It is this expression that ensues from the law of energy conservation in the form of (2.4.9) for a particular case of a single-target machine intended for the conversion if the i^{th} form of energy into the j^{th} one.

Let us show now that it is this efficiency that characterizes the thermodynamic perfection of a machine, i.e. the degree the machine implements those potentials the well of the technically adequate (ordered) energy provides for it. In fact, according to the principle of heat and work equivalency (see 2.1.1) the ordered work W^e done by a cyclic machine related to the algebraic sum of the heats $đQ$ it receives at all stages of the cyclic process is always equal to unity. Relating this work to only that part of the heat Q_1 which is taken from the "hot" well is, from a mathematical standpoint, an implicit technique, moreover, such one that is not always feasible for even the heat engines (in particular, for the processes where temperature rise cohabits with heat rejection). This even more concerns the non-heat engines where the energy wells and sinks occupies the same space (such are, in particular, polarized, magnetized, etc. bodies). At such conditions it is advisable to consider only the actual power of the machine N_j related to that theoretically possible; such a ratio being construed as the power efficiency (see 11.2.1).

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

To show the non-triviality of this concept, let us compare the η_N with the so-called "*exergy efficiency of technical systems for energy and substance conversion*" η_{ex} (Brodiansky, 1991). The latter characterizes the ratio of outlet exergy flow to inlet exergy flow in the machine. The concept of *exergy* as a measure of system working capability relative to the environment is described in Chapter 2 above. For an "extended system" (as including wells and sinks of heat, substance, charge, etc.) the exergy becomes its state function. The exergy flows are equidimensional with power, which links the exergy and power efficiencies. However, the exergy efficiency is not always associated with the conversion of some kind of energy into other one due to the so-called "transit" exergy flows existing. Such is, e.g. the exergy of flow of some substance crossing the reactor and not participating in the chemical transformations therein. Therefore the exergy flow ratio does not yet characterize the effectiveness of the energy conversion in a machine. Besides, the exergy efficiency depends on the exergy value itself as it is commonly construed, i.e. on the reference point choice for some form of exergy or other. This makes the exergy efficiency ambiguous, which restricts the applicability of this working capability function in the efficiency analysis for power and process installations.

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

11.3. Kinetic Equations of energy Conversion Processes. Antisymmetry of Relationships Therein

As shown above, any device converting some i^{th} form of energy into the j^{th} one is a two-flow system, i.e. features energy carrier flows of both the energy being converted J_i and the energy having been converted J_j. The interrelation between flows J_i and J_i is a distinctive feature of the energy conversion processes. One can make sure such an interrelation exists if compare, based on the law of conservation of energy, the expressions of the energy being converted and having been converted:

$$N_i = N_i^{\text{д}} + N_i^{\text{e}} = N_j^{\text{д}} + N_j^{\text{e}}. \qquad (11.3.1)$$

This relationship is an equation of balance between the power input to the machine and power output from the machine. According to this equation the power input N_i is consumed to overcome both the subscript-similar dissipation forces X_i and the “alien” forces X_j, i.e. is not only converted into other form of the useful energy N_i^{e}, but also partly dissipates on the input resistors (this loss is usually designated as N_i^{d}). In its turn, the power N_j converted into the j^{th} form is also partly lost in the secondary equivalent circuit (Fig. 11.1) thereby reducing the output useful power N_j^{e} necessary to overcome the useful forces X_j^{e}. Since by the law of conservation of energy $N_i^{\text{e}} = X_iJ_i^{\text{e}} = N_j^{\text{e}} = X_jJ_j^{\text{e}}$, the flows J_i^{e} and J_j^{e} appears to be interrelated. This interrelation shows itself in the fact that each of the flows J_i and J_j appears to be dependant on both the active forces X_i and X_j acting in the system, i.e. the kinetic equations of the energy conversion process should be written a priori in the form of Onsager’s phenomenological laws (4.1.6):

$$J_i = L_{ij} X_i + L_{ij} X_j \,, \qquad (11.3.2)$$

$$J_j = L_{ji} X_i + L_{jj} X_j \,. \qquad (11.3.3)$$

The number of the phenomenological coefficients in these equations may be reduced by applying the reciprocity relationships to them. However, it is advisable to preliminarily make sure the reciprocity relationships (see 4.5.3) for the energy useful conversion processes bear invariably anti-symmetrical character. To this end let us take into account the difference in sign for the work done to the energy converting device (this work is negative according to the rule of signs in thermodynamics, i.e. $\text{đ}W_i = - X_i dZ_i < 0$) and the work done by this device to the work object $\text{đ}W_j = X_j dZ_j > 0$. With the sign properly considered the exact differential of system exergy may be expressed as

$$dE = - X_i dZ_i + X_j dZ_j \,. \qquad (11.3.4)$$

Repeating the same reasoning as described in paragraph 4.3 when deriving the reciprocity relationships, based on the properties of the inergy E exact differential, one comes to the anti-symmetrical reciprocity relationships:

$$(\partial J_i / \partial X_j) = - L_{ij} = (\partial J_j / \partial X_i) = L_{ji} \,. \qquad (11.3.5)$$

This proof of the so-called Cazimir’s reciprocity relationships differs from those earlier proposed (V. Etkin, 1993) by a particular simplicity and obviousness. The opposite sign of the works đW$_i$ and $đW_j$ taken into account results in kinetic equations (11.3.2)–(11.3.3) taking the form:

$$J_i = L_{ij} X_i - L_{ji} X_j\,, \tag{11.3.6}$$

$$J_j = L_{ji} X_i - L_{jj} X_j\,. \tag{11.3.7}$$

The kinetic equations of such a character (with their terms having different signs) better correspond to the concept of phenomenological (experience-based) laws than initial equations (11.3.2)–(11.3.3). The primary energy carrier flow J$_i$ (e.g. the current in the primary winding of a transformer) is commonly known to decrease as the forces X_j being overcome increase (with approach to "no-load" operation) or, on the contrary, to increase as these forces decrease (with approach to "short circuit" operation). Similarly, the secondary energy carrier flow (e.g. the current in the secondary winding of a transformer) is commonly known to increase as the supply voltage X_i increases and to decrease as the secondary circuit resistance and the X_j decrease.

The proof of the Cazimir's reciprocity relationships adduced here for reversible part of the energy conversion processes is based on the law of energy conservation and, therefore, valid whenever linear phenomenological laws (11.3.2) and (11.3.3) remain valid. This circumstance throws fresh light on the origin of the Cazimir's reciprocity relationships exposing the underneath meaning of the requirements for different parity of forces with respect to time inversion. In fact, for the dissipation forces not changing their signs with time inversion (i.e. for the so-called "α-type forces") the Onsager's symmetry conditions, as shown above, are valid. Whenever a part of these forces have the reversible character (i.e. refer to the "β-type forces"), the Onsager's reciprocity relationships give place to anti-symmetry conditions (11.3.5). At the same time the consideration endeavored here shows that the applicability of the Cazimir's relationships is not actually restricted to the different-parity forces (α and β-type) case. In fact, let us assume dealing with energy conversion processes of purely dissipative character. Such are, in particular, thermal conductivity, electric conductivity, diffusion and viscous friction described by Fourier's, Ohm's, Fick's and Newton's laws and resulting in only the substance and energy transfer. In this case all terms of kinetic equation (4.4.1) describing vector phenomena have the same sign $X_i{\cdot}J_i > 0$ defined by their contribution to dissipative function (5.3.3). In this case reciprocity relationships (4.5.4) defining value and sign of the phenomenological coefficients L$_{ij}$ in linear kinetic equations (4.4.1) give invariably positive values of the phenomenological coefficients $L_{ij} > 0$ in these equations and result in Onsager's reciprocity relationships $L_{ij} = L_{ji}$.

So for linear transfer processes of a purely dissipative character the matrix of phenomenological coefficients is always symmetrical. However, if in a transfer process useful (reversible) energy conversions occur, i.e. work is done against whatever forces other than dissipation ones, the reciprocity relationships acquire other character. In this case phenomena of the "ascending diffusion" type (transfer of components toward their concentration increase), system ordering, etc. are observed. These processes lead to gradients or differences of temperature, pressure, concentration, electric potential, etc., i.e. to deviation of the system from the internal equilibrium state for some of its degrees of freedom, whereas the system in whole is tending toward equilibrium. As a matter of fact, this is the nature of all the so-called "superposition effects" the theory of irreversible processes deals with. As we will make sure hereafter, the effects of such a kind bear anti-dissipative character. The processes of useful conversion of the i^{th} form of energy into the j^{th} one in various machines apply to these effects, too. This substantially extends the applicability of the anti-symmetrical reciprocity relationships (V. Etkin, 1993).

Let us now elucidate what character the relationships between the phenomenological coefficients L_{ij} acquire in a more general case, when these coefficients are some functions of the related thermodynamic forces X_j, so that kinetic equations (11.3.5) and (11.3.7) are non-linear. Applying to them generalized reciprocity relationships (11.3.5) gives for this case:

$$(\partial J_j/\partial X_j) = L_{ij}(X_j) + \Sigma_j X_j(\partial L_{ij}(X_j)/\partial X_j)\ , \qquad (11.3.8)$$

so the generalized reciprocity relationships become:

$$L_{ij}(X_j) + \Sigma_j X_j(\partial L_{ij}/\partial X_j) = L_{ji}(X_{\mathrm{j}}) + \Sigma_j X_j(\partial L_{ji}/\partial X_i)\,.. \qquad (11.3.9)$$

From this it follows that the Onsager-Cazimir's symmetry conditions $L_{ij} = \pm\ L_{ji}$ apply to also those cases when the diagonal phenomenological coefficients

$$L_{ii} = L_{ij}(X_j),\ L_{jj} = L_{jj}(X_i),$$

i.e. are some functions of the forces associated with them, whereas only minor (non-diagonal) terms of the phenomenological laws characterizing the superposition effects are linear. In fact, if the non-diagonal coefficients L_{ij}, L_{ji} are constant, then all expressions within brackets in relationships (11.3.9) become zero. In other words, to meet the symmetry conditions or non-symmetry ones, it is enough the non-diagonal terms in equations (11.3.6) and (11.3.7) responsible for the superposition effects to be linear. We have demonstrably instantiated this by the phenomena of cross diffusion and filtration of ideal gases thru the finite-thickness membrane (see Chapter 11).

It is a matter of interest to confirm the anti-symmetrical reciprocity relationships by specific examples of the useful energy conversion processes. As one of the examples, the thermoelectric generator (TEG) may be considered which operation is based on the Seebeck and Peltier thermoelectric effects. If the ends of different-type conductors A and B are connected and a current source or a load switched into the break of one of them, then in the formed thermo-circuit along with the Thomson's homogeneous effect (electric potential gradient generated along the dead conductor with heterogeneous temperature field) the so-called heterogeneous effects will be observed. One of them arises with the hot and cold junctions of the thermocouple maintained at different temperatures T_1 and $T_2 < T_1$. It consists in the generation of the electromotive force $X_e = -\Delta\varphi$ proportional to the temperature difference $X_q = - \Delta T = T_1 - T_2$ and reaching the maximum value in the absence of the electric current J_e (Haase, 1967):

$$(\Delta\varphi/\Delta T)_{\text{ст}} = \varepsilon_{AB}/T \qquad (J_e = 0), \tag{11.3.10}$$

where ε_{AB} – the so-called thermoelectric force in the thermo-circuit of conductors A and B depending on their nature and the mean temperature of the thermo-element T.

Another effect arises with the current J_e passed thru the junctions and consists in absorbing or releasing by the junction a Peltier heat which flow J_q is proportional to the current J_e and the junction temperature T:

$$J_q = \varepsilon_{AB} J_e T . \tag{11.3.11}$$

With the junctions of the thermo-circuit maintained at different temperatures, the electric current J_e generated will lead to the heat absorption $J_q' = \varepsilon_{AB} J_e T_2$ in junction A and the heat release $J_q'' = \varepsilon_{AB} J_e T_2$ in junction B. Then, in the absence of side processes, the thermo-element becomes similar to a cyclic heat engine with working medium being the free electrons circulating in the thermo-circuit. The dependence of the thermal conductivity λ and the electric conductivity σ_e of the thermo-circuit branches on the fields of temperatures along the conductors (and, thus, on the electric fields associated) makes the TEG phenomenological laws, strictly speaking, non-linear. However, the said non-linearity concentrates in their diagonal terms so that the TEG phenomenological laws become (Haase, 1967):

$$J_q = L_{qq}(X_q)\, X_q - L_{qe} X_e , \tag{11.3.12}$$

$$J_e = L_{eq} X_q - L_{ee}(X_e)\, X_e , \tag{11.3.13}$$

where $L_{qq}(X_q)$, $L_{ee}(X_e)$ – coefficients inverse to, respectively, thermal and electrical impedance of the thermo-circuit branches considered as a function of their mean-integral temperature; $L_{q\mathrm{e}}$, $L_{\mathrm{e}q}$ – cross phenomenological coefficients considered as constant. Here in equations (13.3.6) and (13.3.7) the circumstance is taken into account that with the voltage drop X_e at the TEG output the current J_e on the load and Peltier heat flow rise.

To make sure the anti-symmetry conditions $L_{q\mathrm{e}} = -L_{eq}$ for TEG are met also in the case the coefficients L_{qq} and L_{ee} depend on the associated forces, let us apply the differentiation process corresponding to the left side of equation (11.3.5) to equation (11.2.12). Allowing for constancy of $L_{qq}(X_q)$ at X_q = const gives:

$$(\partial J_q / \partial X_\mathrm{e}) = -L_{q\mathrm{e}}\,. \tag{11.3.14}$$

The same with the (13.3.5) right side gives:

$$(\partial J_\mathrm{e} / \partial X_q) = L_{\mathrm{e}q}\,. \tag{11.3.15}$$

Thus, Cazimir's reciprocity relationships $L_{eq} = -L_{qe}$ for TEG remain valid also with non-linear character of the main terms in equations (11.3.12) and (11.3.14).

A significant consequence from the anti-symmetry of phenomenological coefficients matrix for the useful energy conversion processes is the absence of limitations for the value of the cross phenomenological coefficients, which ensue in TIP from the condition of positive determinacy of their matrix (4.1.9). In fact, at $L_{ij} = -L_{ji}$ condition (4.1.9) is met with any values of the coefficients L_{ij} and L_{ji}. As will be shown a little bit hereafter, this circumstance is of key importance since removes the limitations for efficiency, which is unusual to energy converting systems.

11.4. Similarity Criteria for energy Converting Systems

The unity of phenomenological laws (11.3.6)-(11.3.7) describing different forms of energy conversion processes and their independence on machine hardware implementing such processes allows laying a foundation to the similarity theory of linear energy converting systems. The math model of such a system includes, along with equations (11.3.6)-(11.3.7), the *uniqueness conditions* of processes under investigation. These conditions include:

a) conductivity L_{ij} or resistance R_{ij} coefficients (i,j = 1,2) characterizing the transport properties of the system (analog of the thermo-physical properties in the heat and mass transfer theory);

b) *boundary conditions* defined in this case by the values of motive forces at the current conditions X_i, X_j, or by the flow values at these conditions J_i, J_j;

c) *initial conditions* defined by these force or flow values in "no-load" operation of the machine (at $J_j = 0$) X_{jo}, J_{io}, J_{jo} and in "short circuit" operation (at $X_j = 0$) J_{ik}, J_{jk}. These uniqueness conditions allow forming a number of dimensionless criteria of energy converting systems similarity. Equations (11.3.6)-(11.3.7) are more practical to be expressed in terms of the resistance coefficients R_{ij} in the form:

$$X_i = R_{ii} J_j - R_{ij} J_j \; ; \qquad (11.4.1)$$

$$X_j = R_{ji} J_j - R_{jj} J_j \; . \qquad (11.4.2)$$

Let us consider these equations jointly with the uniqueness conditions. Assuming $J_{jo} = 0$, $X_i = X_{io}$, $X_i = X_{io}$ they can be derived as:

$$X_{io} / X_{io} = R_{jj} / R_{ii} \; ; \qquad J_j = X_{jo} / R_{ji} \; ; \qquad J_j = (X_j - X_{jo}) / R_{jj} \; . \qquad (11.4.3)$$

Similarly for "short circuit" conditions ($X_j = 0$, $J_j = J_{jk}$, $J_j = J_{jk}$) equation (11.4.2) becomes:

$$J_{jk} / J_{ik} = R_{ji} / R_{jj} \; . \qquad (11.4.4)$$

Substituting equations (11.4.1) and (11.4.2) in power efficiency expression (11.2.11) and making a number of transformations using relationships (11.4.3) and (11.4.4) gives:

$$\eta_N = (X_j / X_{jo}) / [1 + R_{ii} R_{jj} / R_{ji}^2 (1 - X_j / X_{jo})]. \qquad (11.4.5)$$

This equation. n allows reducing the uniqueness conditions characterizing the transport properties of the energy machine to a one dimensionless complex:

$$\varPhi = R_{ji}^2 / R_{ii} R_{jj} \, . \qquad (11.4.6)$$

This complex is similar to the relationship between active and reactive resistances known in radio engineering as tuned-circuit Q-factor and coincides (accurate up to a temperature factor) with the "torque-to-weight ratio" $\varPhi$ introduced by A. Yoffe as a generalized characteristic of thermoelectric generators (TEG). Therefore it was termed as a *good quality criterion of machine* (V. Etkin, 1990). Its value ranges from zero to infinity ($0 < \varPhi < \infty$) increasing with decrease of the "active" resistances R_{ii} and R_{jj} (from the dissipation forces) and increase of the "reactive" resistances R_{ji} (from the useful forces). Like the thermal resistances these ones depend on the transport properties of the system (cross-sections and lengths of the heat, substance, charge, etc. transfer lines, properties of the materials applied, transport factors, etc.), i.e., ultimately, on the design perfection of the machine indirectly depending on also its manufacturing expenditures. Based on this, the above criterion could also be termed as a *criterion of design perfection of machine*.

Other dimensionless criterion can be composed of boundary conditions defined by the values of the forces X_{j}, X_{jo} or flows J_j, J_{jk}:

$$B = J_j / J_{jk} = 1 - X_j / X_{j\mathrm{o}}. \qquad (11.4.7)$$

This criterion depends on exclusively the load to the machine ("load current") and ranges from zero at no-load conditions ($J_j = 0$) up to unity at short circuit conditions ($X_j = 0$). Therefore it was termed as a *load criterion of machine* (V. Etkin, 1990, 1991).

Using these criteria expression (1.4.5) can be formed as a *criterion equation of energy conversion process*:

$$\eta_N = (1 - B)/(1 + 1/B\Phi)\ . \qquad (11.4.8)$$

This equation determines the dependence of the thermodynamic criterion of machine perfection upon machine load B at invariable parameters of the technically fit energy source. Thereby one more step has been made on the way to approach the thermodynamic assessment of technical system efficiency to reality.

11.5. Universal Load Characteristics of energy Converters

Like the theory of heat exchange processes similarity, criterion equation of energy conversion processes (11.4.8) allows extending the results of efficiency investigation from some technical systems to other ones (insufficiently explored). To do so, it is advisable to build based on criterion equation (11.4.8) a generalized load characteristic of linear energy converting systems. Such a characteristic is plotted on Fig.11.2. Solid lines show here the power efficiency of the machine η_{N} plotted against the load criterion B for different values of the Q-criterion Φ, while dotted lines – the output power N_j plotted against the load. As follows from the figure, in the absence of energy losses ($\Phi = \infty$) and with quasi-static character of its conversion ($B \to 0$) the machine efficiency reaches, as should be expected, unity. However, in all other cases the power efficiency becomes zero twice: in "no-load" ($B = 0$, $J_j = 0$) and "short circuit" ($B = 1$, $X_j = 0$) operations. This ensues from taking into account, along with the irreversible power interchange and friction, also various "leaks" [1]of power occurring in also "no-load" operation of the machine, in particular, its auxiliary power. With the loads growing and the operation withdrawing from "no-load" conditions the efficiency rises and reaches maximum at a definite load. The efficiency maximums then lie on the same line connecting the operating conditions with "zero" output power ($B = 0$, $\eta_N = 1$ и $B = 0{,}5$, $\eta_N = 0$). The efficiency maximums appeared are explained by varying relationship between the rates of useful and dissipative energy conversions in the system and show that all types of energy converters have the most economical loads usually adopted as *nominal*.

To find the nominal loads $B_н$, let us set the derivative of (11.4.8) with respect to B equal to zero. Some transformations give:

$$B_н = (\sqrt{1+\Phi} - 1)/\Phi. \qquad (11.5.1)$$

According to this expression the power efficiency maximums lie on the same line connecting the points with the load $B = 0.5$ and the efficiency $\eta_N = 1$. The max efficiency value depends in this case on exclusively the Q-criterion value. In fact, substituting (11.5.1) into criterion equation (11.4.8) gives after simple transformations:

$$\eta_N^{\max} = (\sqrt{1+\Phi} - 1)/(\sqrt{1+\Phi} + 1) . \qquad (11.5.2)$$

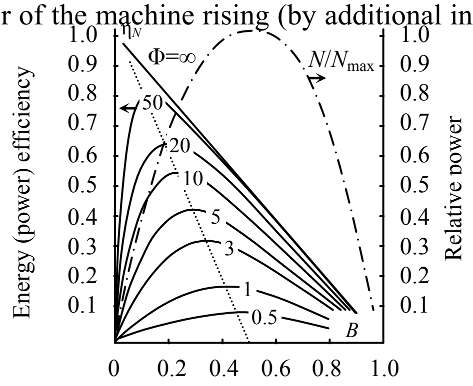


Fig.11.2. Universal Load Characteristics of Linear Systems

As can be seen, with the Φ -factor of the machine rising (by additional investmen

operation of high-efficiency power machines on partial loads is inadvisable. To clarify how the load impacts on the output power of a machine, let us substitute (11.4.8) into the relationship $N_j = N_i\eta_N$:

$$N_j = X_{jo}\, J_{jk} B(1 - B) . \qquad (11.5.3)$$

Since at $B = 0.5$ the power N_j is maximal ($N_j = N_j^{max}$), the value $X_{jo}J_{jk} = 4\, N_j$, and instead of (11.5.3) one can write

$$N_j / N_j^{\max} = 4\, B(1 - B) . \qquad (11.5.4)$$

---

[1] This loss can not be taken into account by traditionally introducing the constant relative efficiencies of work-doing processes since this loss is equal to zero in "no-load" operation.

This plot is also shown on Fig.11.2 with dotted line. From this it follows that at the efficiency $\eta_N = 1$ the output power of any heat engine is equal to zero due to the absence of heat exchange between the heat well and working medium and reaches maximum at a relative load of $B = 0.5$. The efficiency of the engine corresponding to these loads can be found by substituting this load value into (11.4.8):

$$\eta_{(N = \max)} = 1/(2 + 4/\Phi)\ . \qquad (11.5.5)$$

According to this expression the power efficiency of linear energy converters at max power conditions does not exceed 50 % for all forms of energy. For all that the difference in efficiencies of machines with different Φ -factors is leveling off with approaching the max-output power-operating conditions and may become practically indistinguishable. This fact reveals lack of prospects in pursuing high efficiencies for power machines intended for peak-load or power-augmentation operations. Fig.11.2 also shows that with the Φ-factor of a machine rising, the dependence of its efficiency on load grows more perceptible, while the operating conditions of max efficiency and max output power are more and more drifting apart.

The indirect confirmation of the anti-symmetry of reciprocity relationships is another significant conclusion from the load characteristics. In fact, if the Onsager's symmetry conditions were valid for energy converting machines, then they would engender known limitations for the relationship of diagonal and non-diagonal phenomenological coefficients $L_{ij}^2/L_{ii}L_{jj} \leq 1$ or $\Phi = R_{ji}^2/R_{ii}\,R_{jj} \leq 1$ as based on the positive determinacy of phenomenological coefficients matrix (4.1.9). In accordance with Fig.14.2 this means that the exergy efficiency of any energy converters can not exceed ~17.5 % as a limit. Meantime a lot of machines are known with this efficiency exceeding the limit. The said contradiction is eliminated if $L_{ij} = -L_{ji}$ since in this case condition (4.1.9) means just the requirement these coefficients to be positive ($L_{ii}\,L_{jj} \geq 0$).

The universal load characteristics are very convenient when comparing machines of different types for choosing the most challenging of them. Since such an assessment depends on the load of a machine ranging considerably in operation, the comparison needs the load characteristics to be known otherwise being insufficient. Let us show this by example of a hydrazine-oxygen electrochemical current generator (ECG). When operating this fuel cell, a no-load voltage (EMF) was obtained as $X_{jo} = 1.6$ V which decreases with load growth and becomes $X_j = 0.85$ V at a power of $N_j = 2$ kW. Fuel utilization factor and oxidant utilization factor for this unit are $\eta_f = 0.8$ and $\eta_{ox} = 0.9$, respectively (B. Nesterov and others, 1980). To find the ECG power efficiency, let us first calculate the fuel element relative load $B = 1 - X_j/X_{jo} = 1 - 0.85/1.6 = 0.47$. For ideal ECG (with the $\Phi = \infty$) under such a load according to Fig.13.2 η_N does nor exceed 0.51. Allowing for the mean factor of reagents utilization as $\eta_r = 0.85$ gives the effective efficiency for this generator $\eta_e = \eta_N\, \eta_r = 0.51 \cdot 0.85 = 0.43$. Detailed calculations with an exergy flow balance analysis give for this ECG the exergy efficiency $\eta_{ex} = 0.41$ (V. Etkin, 1991), i.e. quite close to η_e. At the same time such a proximate analysis reveals the importance of considering the loads to machines when investigating how far they are challenging. Should in the example considered the ECG effectiveness be estimated thru the max power efficiency $\eta_N \cong 0.85$, the situation would be cardinally outweighed on its side.

11.6. Similarity of Load Characteristics for Real Machines

It is a matter of interest to confirm the similarity of load characteristics for a number of different-type energy converters. As one of the examples, let us consider a space-based propulsion system (SBP). For spacecrafts moving in the absence of air drag and gravity the useful work means the acceleration d**v**/dt of a spacecraft with the mass M under the thrust **R**. This thrust is defined by a known expression (Favorsky and others, 1970):

$$\mathbf{R} = G_m\, \mathbf{w} + F_\text{c}\,(p_c - p_\text{o})\mathbf{n} = G_m\, \mathbf{w}_\text{э} = R_\text{y}\, \mathbf{g}\, G_m\,, \qquad (11.6.1)$$

where G_m – gas flow thru jet nozzle, kg/s; $\mathbf{w}$, $\mathbf{w}_{eq}$ - true and equivalent gas outflow velocity, respectively; p_n , p_o – pressure of combustion products at the nozzle outlet and outside in the environment, respectively, N/m^2 ; $\mathbf{R}_\mathbf{s}$, $\mathbf{g}$ – specific thrust (specific impulse) of the jet engine and gravitational acceleration, respectively.

In the general case of flights in the atmosphere or gravity field the part N_j^d of the converted power N_j works against the environmental resistance forces. Here the useful effect is deemed as the movement of a flying vehicle and the N_j value defined as the scalar product of the thrust **R** by the distance covered per unit time under this thrust. For spacecrafts taking off from the orbit of the Earth with the starting orbital velocity $\mathbf{v}_\text{o}$ this distance is obviously equal to the velocity of spacecraft movement relative to the starting coordinate system $\mathbf{v}_\text{к} = \mathbf{v} - \mathbf{v}_\text{o}$ since at $\mathbf{v} = \mathbf{v}_\text{o}$ no work is done:

$$N_j = \mathbf{R} \cdot (\mathbf{v} - \mathbf{v}_\text{o})\,. \qquad (11.6.2)$$

This expression is applicable also for the engines correcting the satellite orbit and for the flying vehicles taking off from the Earth's surface ($\mathbf{v}_\text{o} = 0$). Taking into account that the vectors **R** and **v** are anti-parallel (so that the problem may be considered as one-dimensional) the output power N_j may be represented as the product of the scalar thermodynamic force $X_j = |\mathbf{R}| =$

R as a motive force or acceleration of the vehicle by the scalar flow $J_j = |\mathbf{v} - \mathbf{v}_o| = v - v_o$ as a generalized velocity of the movement process.

To find the flows and forces of the energy form being converted, let us apply to the first law of thermodynamics for unit mass of moving gases. Under this law, if the processes in combustors and nozzles are running at adiabatic conditions, the specific useful work of the vehicle movement relative to the starting coordinate system is defined by the difference in enthalpy of the combustion products deceleration between the combustor inlet $h_c{}^* = h_c + \mathbf{v}_c{}^2/2$ and the nozzle outlet $h_к{}^* = h_к + \mathbf{v}_к{}^2/2$. According to this the power input to the engine is defined as:

$$N_i = G_m\,(h_c{}^* - h_к{}^*)\,. \tag{11.6.3}$$

This expression may be also represented in the form of the product of the scalar gas flow $J_i = G_m$ as a generalized rate of the process by the scalar thermodynamic force $X_i = -\Delta h^*$. The difference of enthalpies $\Delta h = h_к - h_c$ is known to define the theoretical velocity $\mathbf{w}_t$ of gas outflow from the nozzle ($\mathbf{w}_t{}^2/2 = h_к - h_c$) which relates to the true gas outflow velocity $\mathbf{w}$ thru the relative internal efficiency $\eta_{oi} = \mathbf{w}^2/\mathbf{w}_t{}^2$. Taking into account that for space engines the equivalent gas outflow velocity from nozzles $\mathbf{w}_{eq}$ is substantially equal to the true outflow velocity $\mathbf{w}$, while the absolute outflow velocity for working medium at the nozzle outlet in the starting coordinate system $\mathbf{v}_c$ is equal to the difference between $\mathbf{w}$ and the velocity of the flying vehicle in this coordinate system $\mathbf{v}$, the value X_i may be represented as:

$$h_к{}^* - h_c{}^* = \mathbf{w}\cdot(\mathbf{v} - \mathbf{v}_o) + (1/\eta_{oi} - 1)\,\mathbf{w}^2/2\,. \tag{11.6.4}$$

The augend on the right side of this equation defines the useful component of thermodynamic force $X_i{}^e = \mathbf{w}\cdot(\mathbf{v} - \mathbf{v}_o)$ associated with the vehicle acceleration, while the addend – the dissipative component associated with the initial energy dissipation in the SBP combustors and nozzles (including losses caused by incomplete expansion, dissociation and ionization of working medium, as well as friction loss) $X_i^r = (1/\eta_{oi} - 1)\mathbf{w}^2/2$. The useful force component $X_i^e = \mathbf{w}\cdot(\mathbf{v} - \mathbf{v}_o)$ is proportional to the flow $J_j = |\mathbf{v} - \mathbf{v}_o|$ thru the proportionality factor $-R_{ij} = |\mathbf{w}|$, while the dissipative component – to squared velocity (and, consequently, squared flow $G_m = J_i$). This causes non-linearity of the relationship $X_i = X_i(J_i)$. However, this non-linearity is concentrated in the diagonal term that may be represented as $X_i^r = R_{ii}G_m = [(1/\eta_{oi} - 1)\mathbf{w}^2/2G]G_m$, where the diagonal phenomenological resistance coefficient $R_{ii} = (1/\eta_{oi} - 1)\mathbf{w}^2/2G_m = R_{ii}(G_m)$, i.e. is a function of the flow associated.

Similarly, the thrust $X_j = R$, in the general case of flights in the atmosphere or gravity field, may be represented as a sum of the useful component

$X_j^{e} = Gw$ associated with the vehicle acceleration and proportional to the flow $J_i = G_m$ thru the proportionality factor $R_{ji} = w$ and the dissipative component X_j^{r} associated with the atmosphere resistance to be overcome and depending on the flight velocity $J_j = |\mathbf{v} - \mathbf{v}_o|$. This dependence is also nonlinear, but may be represented in the pseudo-linear form $R_{jj}(J_j)J_j$ thru the proportionality factor $R_{jj}(J_j)$ depending on the velocity increment Δv.

Thus the SBP phenomenological laws may be expressed in informal variable as:

$$-\Delta h^* = R_{ii}(G_m)\, G_m - \mathbf{w}\cdot(\mathbf{v} - \mathbf{v}_o)\ , \qquad (11.6.5)$$

$$R = w\, G_m - R_{jj}\, (\mathrm{v} - \mathrm{v}_o)\ . \qquad (11.6.6)$$

Here the negative sign of the second term in equation (13.6.5) allows for the opposite direction of the force $\mathbf{X}_i$ and the flight velocity $\mathbf{v} - \mathbf{v}_o$. In accordance with this equation at Δh^* = const increasing the flight velocity demands increasing the working medium flow, which is the reality. Similarly the negative sign of the second term in equation (11.6.6) allows for the fact that at the constant thrust and constant flow of working medium G increasing the flight velocity $\mathbf{v} - \mathbf{v}_o$ demands increasing the propulsive jet velocity **w**, which is quite natural, too. Such a character of the SBP phenomenological laws leads to the anti-symmetry of reciprocity relationships. In fact, applying relationships (11.3.5) to equations (11.6.5) and (11.6.6) gives:

$$(\partial X_i / \partial J_j) = - R_{ij} = (\partial X_j / \partial J_i) = R_{ji} = w\ . \qquad (11.6.7)$$

The fact that the non-linear laws of mechanical energy forms conversion in SBP are quite within the frames of thermokinetics substantially expands its applicability and allows extending its analytical methods to complex mechanical systems, which seems to be quite important (Burdakov, 1985).

Now let us find the SBP power efficiency using the above-obtained expressions for input and output powers of the machine. Simplifying expression (11.6.4) as:

$$h_{к}^* - h_{c}^* = \mathbf{w}^2/2\eta_{oi} + \mathbf{v}^2/2\ , \qquad (11.6.8)$$

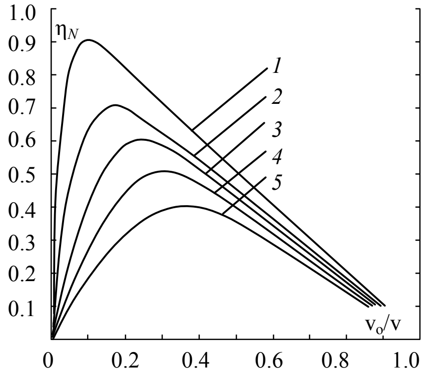
gives that the SBP power efficiency η_N takes the form:

$$\eta_N = \mathbf{w}\cdot(\mathbf{v} - \mathbf{v}_o)/(\ \mathbf{w}^2/2\eta_{oi} + \mathbf{v}^2/2)\ . \qquad (11.6.9)$$

At $\mathbf{v}_o = 0$ and $\eta_{oi} = 1$ this relationship goes over into a known expression for the propulsion (thrust) efficiency (Alemasov, 1962). This differs from the SBP total efficiency by the velocity increment for the flight time ($\mathbf{v} - \mathbf{v}_o$) it features instead of the absolute flight velocity **v** in the SBP total efficiency. Thereby it is taken into account that maintaining the flight velocity $\mathbf{v} = \mathbf{v}_o$ in the absence of the air drag does not demand any work. Expression (11.6.2) can be reshaped to a more general form by introducing the relation $B = v_o/v$ as the SBP load criterion:

$$\eta_N = 2B(1 - B)/[B^2(\mathbf{w}/\mathbf{v}_o)^2/2\eta_{oi} + \mathbf{v}_o/\mathbf{w}]\,. \tag{11.6.10}$$

The above relationship is correspondingly plotted on Fig.11.3. It is easy to see that its character completely corresponds to the universal load characteristics on Fig.11.2 despite the non-linearity of SBP phenomenological laws (11.6.5) and (11.6.6). Fig.11.3 shows that the machine efficiency as a function of the relative load B (flight relative velocity $\mathbf{v}_o/\mathbf{v}$) becomes zero twice: at $B = 0$ and $B = 1$. The first case corresponds to near-the-light speed flights when a further flight speed increment becomes impossible ($J_j = J_{jk}$ – just like at “short-circuit” conditions). Such a situation is of theoretical interest for the spacecrafts with the solar sails (Favorsky and others, 1970), which thrust drops to zero as the flight speed is approaching the light speed.



1, 2, 3, 4, 5 – $\mathbf{R}_s/\mathbf{v}_0$ = 1.0; 0.5; 0.2; 0.15; 0.1

Fig.11.3. Generalized Curves SBP Efficiency – Fight Speed

The opposite case (B = 1) applies to any spacecrafts at the moment they are taking off, when the flight speed is equal to the starting one ($\mathbf{v} = \mathbf{v}_o$). With the flight speed increasing the efficiency curve reaches its peak value which position depends on the $\mathbf{v}_o/\mathbf{w}$ ratio and the perfection degree of the internal processes in the engine.

As another example let us compare the individual characteristic of a thermionic energy converter (TEC) built based on the universal load characteristic (Fig.11.2) for a known Q-criterion Φ with the power and effective efficiency of one of such converters plotted experimentally against its output voltage Δφ (M. Tribus, 1970). When investigating the TEC Q-criterion, we will proceed from the TEC characteristics, according to which the TEC effective efficiency η_e does not exceed 11% at the cathode and anode temperatures 2,200^{0}C and 30^{0}C, respectively. Proceeding from the fact that at these temperatures the theoretical efficiency of ideal TEC $\eta_t^K \approx 0.88$ gives the power efficiency η_N =12.5% corresponding to the above effective efficiency. In principle, this is enough to choose from the curves on Fig.11.2 and to plot a TEC individual load curve. To be able to compare it with the experimental curve of the effective efficiency η_e against the TEC output voltage, it is necessary to convert it into a generalized form of $\eta_N = \eta_N(B)$. This may be easily done by relating the TEC output voltage $\Delta\varphi$ to the "no-load" voltage (TEC EMF) $\Delta\varphi_0 = 0.9$ V since for the TEC $B = 1 - \Delta\varphi/\Delta\varphi_o$. The results of such a conversion are illustrated on Fig.11.4. Here the light dots denote the experimental values of effective efficiency, while the black dots – the experimental values of the TEC specific power. As follows from the figure, in general, the character of the curves $\eta_N = \eta_N(B)$ and $N = (B)$ well complies with the universal load characteristics.

The universal character of the load characteristics on Fig.11.2 may be further instantiated by the experimentally-found load characteristics of vortex-type gas energy separators based on the Ranque-Hilsch effect. The phenomenon of homogeneous gas energy separation into "cold" and "hot" flows known as the "vortex effect" or Ranque-Hilsch effect was discovered in 1933 by the French metallurgical engineer J. Ranque and then more thoroughly investigated by R. Hilsch in 1946. The vortex tube (VT), where the Ranque-Hilsch effect appears, is a smooth cylindrical or conical tube with one of the ends closed by a diaphragm having a central hole and the other end provided with a throttle having a size-controllable annular slot positioned around the tube periphery. The tube is equipped with tangential nozzles positioned mostly near the diaphragm. Compressed thermally homogeneous gas is fed thru the nozzles to the tube forming two vortices there drifting in the opposite directions inside the tube. One of them, peripheral, rotates with about constant rotational velocity $\mathbf{v}_\tau = \omega r = \mathrm{const}$ (where ω – angular velocity; r – vortex current radius) and drifts toward the throttle leaving it notably heated if throttled down enough; while the other vortex, central, rotates by the laws of rigid body $\mathbf{v}_\tau/r = \mathrm{const}$ and drifts toward the diaphragm leaving it cooled. The cooling effect rate may reach $(60\text{-}70)^0$C and more, which causes a keen interest in the vortex effect from both theoreticians and empirics. Vast information is presently available on experimental investigation of this effect. Fig.11.5 demonstrates a piece of the most complete data of full-scale tests made on the vortex tube (Biruk, 1993). Here the dotted lines denote the separation factor $\eta_T = 1 - T_h/T_c$ (where T_h, T_c – absolute temperatures of the "hot" and "cold" flows, respectively) plotted against the relative load of the machine defined by the cold air share $\mu \equiv B$ for various ratios between the gas pressures upstream and downstream of the nozzle $\pi = p_1/p_2 = 2, 5, 7$. In that case the relative

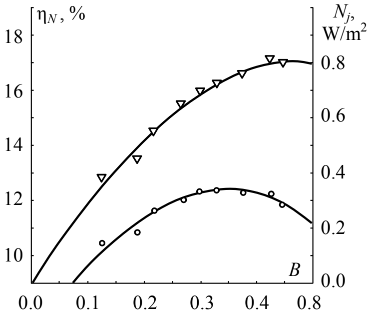


Fig.11.4. Load Characteristics of Thermionic energy Converters

load value ranged from zero (at “no-load”) to unity (“short circuit” analog). The solid lines on the figure denote the vortex tube “cooling capacity” $\mu\eta_T$ related to primary gas flow unit and measured by the product of cold air share μ and the temperature separation factor η_T and plotted against the load $B \equiv \mu$. As this value is nothing else but the outlet gas flow exergy per gas flow unit, the curves on Fig.11.5, at π given, are nothing else but the individual load characteristics of the vortex tube plotted to a certain scale. It can be easily seen that the curves $\eta_T = \eta_T(B)$ and $\mu\eta_T = \mu\eta_T(B)$ in their character satisfactorily reproduce the universal load characteristics of linear energy converting systems $\eta_N = \eta_N(B)$ and $N = N(B)$ despite the non-linearity of gas expansion in the nozzles of the vortex separators. It is significant that with increasing π (Φ -criterion analog) the peak values of the separator economical efficiency η_T drift toward the relative loads $B = \mu$ reducing, whereas the capacity peak values $B\eta_T$ fall at same value B – just as it follows from the theory of similarity of energy conversion processes. Thus the non-linearity of the processes running in the vortex tube tells on mostly the locations of the said peak values. In particular, the location of the capacity peak changes from $B = 0.5$ to $B = 0.55…0.6$. This allows using the deductions of thermokinetics for analysis of real machines thus facilitating the choice of their optimal operating conditions.

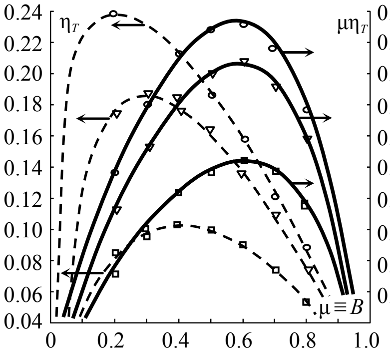


Fig.11.5. Load Characteristics of vortex-type gas energy separators

The fact the max efficiency and max power operating conditions exist is also confirmed by the efficiency curves of electro-technical energy converters, characteristics of pumps and fans, velocity characteristics of internal combustion engines, etc. All this evidences that thermokinetics correctly mirrors the general mechanisms of non-static energy conversion processes thus moving one step further toward the reality.

Chapter 12

THEORY OF ENGINEERING SYSTEMS PRODUCTIVITY

Perceiving the rate and the productivity of real processes as one of their efficiency criteria has revealed two more branches in thermodynamics of the XX$^{\text{th}}$ century along with the theory of irreversible processes (TIP) and called, respectively, “thermo-economics” and “finite-time thermodynamics” (FTT). Of the two branches, the former originates in the M. Tribus’s and his research fellows’ works (Tribus, Evans, Crellin, 1966) and is intended for commensuration of savings in current fuel and materials due to machine efficiency upgrade with the investments associated. Introducing economics elements in thermodynamics modifies the engineering system efficiency criteria themselves since not the maximum of efficiency optimizes now the parameters of engineering systems, but the minimum of their planned costs. This direction involving also the heat exchange theory along with thermodynamics was further developed and widely applied in our country largely due to the works by A. Andrushchenko and his school (1974).

The second branch assigned a top priority to define conditions to obtain maximal economic efficiency considering restricted contact of working medium in power plants with heat well and heat sink. This is the theory that first and most generally framed the question of interrelation between power (productivity) of engineering systems and their thermodynamic efficiency, i.e. of essentially the extreme capabilities of real processes given their irreversibility. However, this theory in the available form is suitable for only the machines operating under maximum power conditions. In this context quite topical is the question how to construct a more general theory of engineering systems productivity, which should comprise both of the said branches as particular cases and relate to the classic theory of heat engines the same way as dynamics to statics.

12.1. Synthesis of Thermokinetics with Thermoeconomics

The abovementioned independent development of the three branches of present-day thermodynamics (theory of irreversible processes (TIP), thermo-economics and finite-time thermodynamics (FTT)) is largely conditioned by the difference in efficiency criteria for the real (non-static) energy transfer and conversion processes theses branches investigate. These criteria are as follows: for TIP – minimum of entropy generation in a system σ_s (De Groot, Mazur, 1964); for thermo-economics – minimum of machine planned costs $З_p$ = min (A. Andrushchenko, 1963; M. Tribus, 1970); for FTT – maximum of machine output power N_j = max (Barrer, 1982;

Rudenko, Orlov, 1984). Creation of thermokinetics as a unitary thermodynamic theory of real processes and the associated theory of similarity of power and processing plants allows including load and productivity of such machines in the number of the parameters being optimized. This facilitates elaborating a unitary efficiency criterion for power and processing plants and creating on its basis a theory of engineering systems productivity considering not only thermodynamic parameters, but also operation condition and cost.

Let us adopt for an objective function when optimizing the operation conditions of operating power and processing plants the maximal benefit Π defined as the difference between the sales income (VAT and excise tax not included) and the production and sales expenses as included in the production cost. Dividing, as usual, the production expenses into the variable depending on production output *Э* and the conditionally constant Є and relating the variable expenses to the production output the objective function may be represented as:

$$\Pi = (\hat{g} - \text{œ})\text{Ə} - \text{Є} = \max, \tag{12.1.1}$$

where $\hat{g}$ means the finished product unit price, while œ – variable component of unit cost.

Let us consider this expression together with the generalized relationships between power and productivity of machines offered by the theory of their similarity. Let us consider, in N – machine mean power, τ – machine operating hours; $\hat{g}$ – power release price, \$/kWh; $\hat{g}^*$ – value close to fuel cost component in total power cost, \$/kWh). Representing the fuel cost component $\hat{g}^*$ as the product of the fuel price þ_f (\$/kg) by the fuel rate $b_{\text{т}}$ (kg/kWh) and expressing the latter in terms of its minimal (theoretical) value $b_{\text{т}}^{o}$ (corresponding to $\eta_N = 1$) as $b_{\text{т}} = b_{\text{т}}^{o}/\eta_N$ the objective function may become:

$$\Pi = (\hat{g} - b_{\text{т}}\text{þ}_f) N \tau - \text{Є} = \max . \tag{12.1.2}$$

Let us now express this objective function in terms of the machine load B using the generalized relationships relating the machine power and efficiency η_N with load criterion (11.4.8):

$$\Pi = [(\hat{g} - b_{\text{т}}\text{þ}_f)(1 + 1/B\Phi)/(1 - B)]\, \mathrm{N}_{\max} B(1 - B) - \text{Є}. \tag{12.1.3}$$

Maximizing this expression as the load function B by equating its derivative to zero gives after some transformations:

$$B_{\text{opt}} = 0{,}5(1 - \eta_N \text{œ}) . \tag{12.1.4}$$

where œ = $b_{\text{т}}$ $þ_{f}/\hat{g}$ –fuel component share in the total electric power price.

Substituting (12.1.4) into (11.5.4) gives an expression for the machine power economically most advantageous:

$$N_{opt}/N_{max} = 1 - (\eta_N œ)^2 \qquad (11.1.5)$$

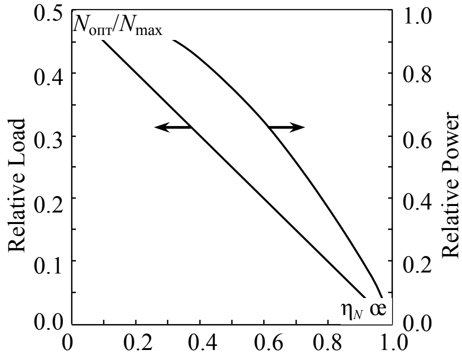


Fig. 12.1. Operating Conditions Economically Most. Advantageous for Power Plants

According to this expression, the less the fuel component of power price (and more generally – variable costs component in product price) is and the less economical the machine is, the closer the nominal power approaches its peak value. The relationships (12.1.4) and (12.1.5) are more demonstrably plotted on Fig. 12.1. The complex η_N œ values varying from zero to unit are plotted here on the abscissa, while the machine relative loads and powers economically most advantageous are plotted on the ordinate. As follows from the figure, with œ → 0 or $\eta_N \to 0$ the optimal load $N_{opt} \to N_{max}$. This result is characteristic for machines on renewable energy sources (hydropower stations, tidal, wave, wind, solar and geothermal power stations) and complies with the efficiency criteria of finite-time thermodynamics. On the contrary, with cost factors neglected ($c_{\text{т}} \approx 0$) quasi-static processes ($B \approx 0$) appear to be most advantageous. This result complies with the thermodynamic approach where the machine efficiency is the only criterion. Machines with a considerable variable costs share occupy an intermediate position. E.g., for thermal power stations with a power efficiency of $\eta_N \approx 0.45$ and a fuel component in product price of œ ≈ 0.6 the optimal load B_{opt} is equal to 0.36 and close to the nominal one corresponding to the utmost economic efficiency of a machine with the Φ-factor $\Phi \approx 4.5$ (Fig. 11.2). This result complies with the efficiency criterion of thermokinetics since for a machine with a specified productivity (operating to a specified load curve) the peak of benefit corresponds to operating conditions with minimal specific fuel rates $b_{\text{т}}$ = min. Thereby thermokinetics as if "lays a bridge" between classic thermodynamics, thermo-economics and finite-time thermodynamics and allows to put further questions of optimal operating conditions definition for power and processing plants of various types.

12.2. Nominal Operating Conditions for Power Units

Including load in the number of factors to be optimized enabled determination that maximum of efficiency for power and processing plants of various kinds was far from being always corresponding to their peak power. In particular, for a big group of thermal power plants operating to a specified load curve B_{opt} corresponds to nominal operating conditions (with minimal fuel rate). This demands the loads to be optimally distributed between the power units of a thermal power station. The solution to this rather laborious problem is considerably facilitated due to the available universal load curves for energy converting systems and due to the possibility to plot on their basis individual load curves for various types of power units despite a restricted scope of information. To do this, the data of full-scale test on all power units or aggregates should be presently available. To obtain such data, considerable time and costs are needed; therefore such tests are extremely seldom with the results often becoming obsolete yet in the period between overhauls. Besides, the calculations of fuel rate increment per unit power increase for any operating conditions of a machine the existing methods of load distribution are based on are so complicated and laborious that their application is far from being always paid back. Therefore in practice a known principle has to be followed, which reads that more economical machines should be loaded first of all. Nevertheless, this statement is far from being always true. Let us assume there are two power units on a thermal power station with the same installed power and good quality factors Φ = 4.7 and 3.0. Then according to criterion equation (12.4.8) the relative load of the first power unit being increased from 0.2 to 0.3 will increase its power efficiency η_{N} from 0.387 to 0.409, i.e. by 0.022, whereas for the less economical unit with Φ = 3.0 this efficiency will increase from 0.30 to 0.331, i.e. by 0.031. Hence, the second power unit being loaded will provide a higher both absolute and relative increase in economic efficiency of the entire thermal power station and a lower increase in its fuel rate. In other words, everything depends on the working point position on the universal load curves of a machine. Fig. 11.2 visually demonstrates this statement. E.g., the load of a machine operating with maximal η_{N} being increased, its economic efficiency may even decrease, whereas the same for another machine operating under loads considerably inferior to nominal will cause steep increase of its economic efficiency. In this context the visualization of operation conditions for power system units in the form of an array of working points on the universal curve of the Fig.11.2 type facilitates the solution to the problem posed since allows, subject to reasonable accuracy of the prognostic estimates, cutting the expenses to conduct relevant tests and calculations.

To illustrate plotting and using individual load curves, let us consider an arbitrary condensing steam turbine plant. The individual load curve for such a machine can be plotted in linear approximation as based on the information about its operation at one of the operating conditions with subsequent reconstruction of the efficiency and power curves configuration on the basis of criterion relationships or universal curves. A working point may be found on Fig.14.2 by several ways. Firstly, this may be done based on the records of the power unit mean load for some time period and of equivalent fuel consumptions for the same period, which allows calculating the equivalent fuel rates $b_{т}$ followed by determining the machine exergic efficiency $\eta_N = 3600/b_{т}\,þ_f$ in terms of the exergy $e_{т}$ known. The relative load B can be herein found according to (12.1.4) as the ratio of generator currents at the present / short circuit operating conditions. E.g., for the ТФ-series 63MW generators the rated current and short-circuit current are 7,210A and 24,000A, respectively, i.e. their relative load at nominal conditions is 0.3. Ultimately, a working point can be also found by known quality factor Φ of the steam turbine plant, which can be estimated as based on its recorded cycle parameters. Let the steam turbine plant be operating, for example, at mean thermodynamic temperatures of the heat well (fuel combustion products) and heat sink (circulating water) equal to $T_{\mathrm{h}} = 1{,}120\mathrm{K}$ and $T_c = 295\mathrm{K}$. If the mean thermodynamic temperatures of heat application and heat abstraction in cycle are in this case $T_1 = 625\mathrm{K}$ and $T_2 = 305\mathrm{K}$, respectively, while the effective efficiency of the steam turbines $\eta_{\mathrm{oe}} = 0.87$, then neglecting the feedwater pumps operation the quality factor of the entire steam turbine plant may be assessed in linear approximation by replacing the resistance relationship by the relationship between the adequate integral forces. As a result of calculation the quality factor for the steam turbine plant under consideration can be found according to (11.3.6) as $\Phi = 4.57$. For this value the load economically most advantageous is according to (11.5.1) $B_n = 0.297$, while the peak value of the power efficiency $\eta_N = 0.40$. Thus rather simple calculations allow assessing the quality factor of an operating power plant and plotting, as based on the quality factor, (in linear approximation) the total load curve of this power plant without additional experiments. In that way the similarity theory-based express methods channel the load optimal distribution issue in the practical direction.

12.3. Optimal Overload Degree of Power and Processing Plants

We have considered above the case when the peak of economic efficiency of power and processing plants was associated with their operation under the relative loads either maximal or close to such. However, according to Fig. 11.2, there is a rather wide spectrum of operating conditions in-between those of maximal power and maximal economic efficiency usually taken as nominal, which may be called overloading or boosting. Such operating conditions are quite characteristic for overland, air and space vehicles. They occur in also stationary power plants intended for irregular load curve operation. However, the choice of power augmentation optimum has not been hitherto considered with due regard. In power engineering this is explained so that the nominal operating conditions of power units are close to their limit power (according to the technical operation standards an electric generator may be overloaded for several seconds to several minutes); in other cases the interest in the problem is restricted because power units operate according to an assigned load curve or because the thermodynamic mathematical tool can not be applied to their analysis in finite-time format. It can only add to the interest to consider these issues from the thermokinetic positions.

According to expression (12.1.4) the economically most advantageous load B^{opt} at the utmost high fuel cost component œ = 1 is defined by exclusively the efficiency of a machine and corresponds to minimal fuel rate. Such loads are usually taken for the nominal B_n. For them the ratio B^{opt}/B_n is evidently equal to unit (1). With œ decreasing at Φ = const (and, hence, at B_n and η_{ex} being invariable in the nominal operation) the optimal loads increase, and the machine operation becomes economically justified for loads exceeding those nominal, i.e. in the so-called augmentation operation. The economically most advantageous augmentation level evaluated by the B^{opt}/B_n ratio can be found from (12.1.4) and, for a higher degree of generality, expressed as a function of the quality factor Φ. Such a relationship is illustrated on Fig.12.2. According to the generalized graphs plotted therein the economically justified overload degree for power and processing plants increases with their quality factor. If, e.g., for steam turbine plants with the quality factor $\Phi = 3...4$ at the fuel cost component in the total power price œ ≈ 0.5 the economically most advantageous overload degree is 1.25…1.35 (which means the power overload by only 4.1% at $\eta_N \approx 0.4$ and according to (12.1.4), then the problem of using overload operations is well actual for highly economical processing plants.

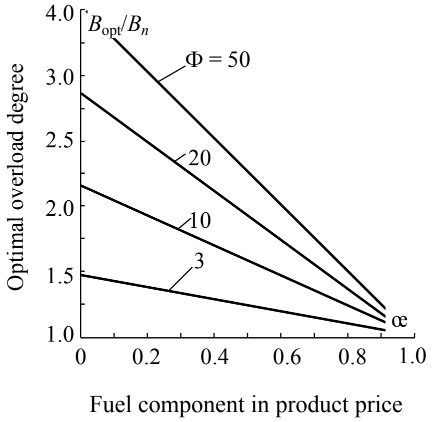


Fig.12.2. Optimal Overload Degree for Power Plants

Let us consider, for a specific example, an electrolysis plant to extract hydrogen and oxygen from water, which exergy analysis is described by Nesterov in his work (1980). The plant consists of an electrolysis cells battery, gas-liquid solution separation units, electrolysis gas purification and dehydration units, heatexchangers and pumps. The power supply to the plant includes the electric power N_{el} and the flows of commercially suitable energy (exergy) with initial reagents Ex_p. The plant productivity in whole is defined by the amount of the hydrogen and oxygen produced. Its energy (exergy) equivalent is construed as the power N_j defined by the flows of commercially suitable energy of electrolysis products Ex_{pr} and heat carriers Ex_h. In the scheme under consideration water is fed to the plant from outside, while gases are removed from the battery together with electrolyte. The plant power N_j = 1,500 W, battery voltage 1.95 V. The ambient air temperature and pressure are T_o = 298 K, p_o = 0.1013 MPa, respectively. To represent the operational conditions of such a plant in terms of the similarity theory, let us consider the electrochemical reactions running in the anode and cathode parts of the electrolysis elements:

$$4\ OH^- - 4\ e = O_2 + 2\ H_2O\ (\Delta\varphi = +0.401\ B), \qquad (12.3.1)$$

$$4\ H_2O + 4\ e = 4\ OH^-\ (\Delta\varphi = -\ 0.83\ B), \qquad (12.3.2)$$

where $\Delta\varphi$ – potential difference across the proper electrode, e – designation of electron as a system component.

As follows from (12.3.1) and (12.3.2), EMF of this reaction is equal to 1.23V, which corresponds to a battery power efficiency of $\eta_N = 0.63$ (a more detailed calculation gives $\eta_N = 0.621$). In this case the voltage drop across the battery internal resistance is 0.72 V, which corresponds to the relative load $B = 0.72/1.95 = 0.37$. According to the universal load curves such parameters refer to a plant with the quality factor $\Phi \approx 50$. The optimal overload degree for this plant according to Fig.14-2 is 2.5…2.25 at œ ≈ 0.4 ÷ 0.5. As a matter of fact, the plant operates with even higher overload. Indeed, for a plant with $\Phi \approx 50$ according to the universal curves on Fig.13-2 the nominal operating conditions are associated with the relative load $B \approx 0.12$ and $\eta_N = 0.77$. Thus the plant under consideration actually operates under a threefold overload relative to the most economically advantageous operating conditions, which is economically justified subject to a moderate price for electric power (œ ≈ 0.2). Hence, this plant has some reserves in economic efficiency upgrade. Anyway, this example tells it is expedient to modify the operating conditions of processing plants according to market-determined prices for finish products and electric power. This fact taken into consideration at market economy may become an extra incentive to maintain optimal operating conditions of equipment and to update the existing power and processing plants in order to extend their overload capabilities under the finished product deficiency.

12.4. “Cruising Speed” Operation of Transport Vehicles

For transport vehicles of a wide spectrum the peak efficiency as per condition (12.1.4) does not correspond any more to the peak power of their propulsion systems. The point is that the power augmentation entails increasing the fuel rate and the fuel load required to deliver a cargo in self-sufficient sea or air freight, which results in the adequate reduction of the net load being carried, i.e. in the drop of the vehicle capacity. The reduction in income from vehicle running thus caused can be accounted for in (12.1.2) by adequately increasing the costs for transportation of fuel itself. In this case in (12.1.2) along with the term $b_{\text{т}}\text{þ}_{\text{f}}$ characterizing the fuel component in the variable costs an additional cost summand will appear proportional to the transportation power inputs with a proportionality factor equal to the unit fuel transportation cost þ_{tr}:

$$\Pi = [\hat{g} - b_{\text{т}}(\text{þ}_{\text{f}} + \text{þ}_{tr})]\, N\tau - \text{€} = \max . \qquad (12.4.1)$$

Due to this the optimal load on the vehicles’ propulsion systems defined by expression (12.1.4) will decrease a little as compared with the peak power operating conditions and will be now associated with the cruising speed of a ship or aircraft corresponding to the minimal fuel rate and, hence, to the minimal mass of the vehicle itself. Minimum mass of a transport vehicle at the given power of its propulsion system will evidently provide the transportation of the maximal cargo, i.e. corresponds to the maximal capacity of the vehicle. Therefore, the problem of transport vehicle mass minimization is one of the most important design and operational targets. This issue is of utmost importance for space vehicles where the net mass of the cargo being transported often defines the range and duration ability of the vehicle, i.e. the feasibility of particular space programs.

Let us consider for example the total mass minimization problem for a space vehicle proceeding from the only requirement to deliver a specified net cargo while moving in a specified path (Etkin, 1996). Such an approach assumes the definition of the so-called characteristic velocity of the space vehicle v as the sum of its velocity increment magnitudes Δv_{i} at particular stretches of its path. For space vehicles starting off from the satellite orbit this velocity is usually counted off from the orbital velocity and defined by the Tsiolkovsky’s formula:

$$\mathbf{v} = \mathbf{w} \ln(M_k/M_{\text{o}}) , \qquad (12.4.2)$$

where M_k, M_{o} – initial and final mass of the flying vehicle (with propulsions on and off), respectively; $\mathbf{w}$ – jet stream velocity assumed constant.

Since $M_о = M_д + M_п = M_к - M_т$, relationship (12.4.2) gives:

$$M_т = (M_д + M_п)[\exp(v/w) - 1] . \qquad (12.4.3)$$

Then the total mass of the space vehicle is equal to:

$$M_к = (M_д + M_п) \exp(v/w) . \qquad (12.4.4)$$

Now let us express $M_д$ in terms of the specific (related to the jet stream kinetic energy) mass of the propulsion system $\gamma_д = 2M_д/Gw_c^2$. Then:

$$M_к = (\gamma_д G w_c^2/2) \exp(v/w) + M_п \exp(v/w) . \qquad (12.4.5)$$

Equating the derivative of this expression with respect to the velocity w to zero under the assumption of **v**, G, $\gamma_д$ and $M_п$ being constant gives:

$$2w - v - M_п \mathbf{v}/\mathbf{w}^2 G\gamma_д = 0 . \qquad (12.4.6)$$

Introducing for convenience the net cargo share $\rho_п = M_п / M_д^{opt}$ as the ratio of the cargo mass $M_п$ to the optimal mass of the propulsion system (at $w = w_{opt}$) and considering that $2M_п v/ G\gamma_д w^2_{opt} = \rho_п v$ gives finally:

$$(w/v)_{опт} = (1 + \rho_п)/2 \text{ или } R_{уд}^{опт} = (1 + \rho_п)v/2g, \qquad (12.4.7)$$

where $R_{sp} = w/g$ – the so-called specific jet thrust (g – gravitational acceleration).

According to this equation the optimal specific thrust value R_{sp}^{opt} at v, G, $\gamma_д$ and $M_п$ = const does not depend on the flight duration, propulsion system efficiency and specific gravity and is defined by exclusively the flight path (v value) and the cargo net weight. That resulted from a more general problem definition, which did not assume the constancy of the propulsion system power N, full thrust R and the specified flight duration τ and demanded a minimal scope of initial data. The solution to the problem in the form of (12.4.1) and (12.4.2) has the same general character and is valid regardless the type of the jet engine, its design and size features. At the same time such an approach to choosing R_{sp}^{opt} leaves enough freedom to choose the propulsion system power $N_p = Gw^2/2$, working medium consumption G and propulsion full thrust R, and, hence, the active propulsion time τ. It is significant that the value R_{sp}^{opt} defined by (12.4.2) is considerably lower than that found under constancy of the jet propulsion full thrust R and the specified active flight duration τ and considerably closer to the optimal relationship between the jet outflow and flight velocities $(w/v)_{opt}$, which is equal to unit and corresponds to the peak value of the jet engine power efficiency.

Fig.12.3 illustrates the relationship according to expression (14.4.5) between the spacecraft mass $M_{к}$, net cargo mass $M_{п}$ and the velocity ratio w/v. For a better generality the values $M_{к}$ and $M_{п}$ are related therein to the spacecraft optimal mass $M_{ко}$ calculated from equation (19.4.5) in the absence of the net cargo and, thus, with the optimal ratio $(w/v)_{opt} = ½$. As follows from the figure, the minimal ratio $M_{к}/M_{ко}$ (optimal R_{sp} = w/g) with the net cargo share increasing shifts, as should be expected, toward higher values of the outflow velocity. However, the deviation from the optimal ratio w/v results, at the conditions accepted, to a steeper increase of the $M_{к}/M_{ко}$ value than at the constant thrust of propulsions. The spacecraft mass increases especially sharply with the w/v ratio reaching some minimal value, which evidences that the application of engines with a specific thrust below the said value is unpractical. E.g., for the "round trip" flights to Venus or Mars (when the minimal characteristic velocity is equal to 3.7-3.8 km/c (Yavorsky and others, 1970)) with the net cargo mass $M_{п} = M_{д}^{opt}$ the application of a liquid-propellant rocket engine on components of the "oxygen-gasoline" or "nitric acid-kerosene" types (with a specific thrust of 260-300hp) is practically excluded. Engines of other types have to be used for these purposes, in particular, the nuclear-fission rockets with specific thrusts of 750-800hp on hydrogen operation. The more general relationships obtained here between the spacecraft mass and velocity parameters may be useful for also determining the ranges of required specific and full thrusts, propulsion system type and power, as well as a number of other parameters of a space rocket engine for particular space flights.

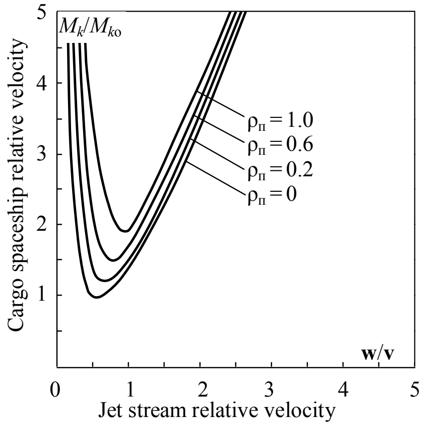


Fig.12.3. Spacecraft Specific Thrust and Net Cargo Optimization

12.5. Peak Power Reach Conditions for Heat Power Plant

Classic thermodynamics is known to have posed and solved the problem of determining the most economical thermodynamic cycles (with maximal thermal efficiency or heat transformation ratio) within a specified temperature range. These are known to be the ideal Carnot cycles. Classic thermodynamics characterizes with a conclusion that the maximal efficiency of heat engines does not depend on the properties of the working medium (its state equations) and is defined by solely the temperature interval within which the cycle is realized. However, the duration of real thermodynamic processes is finite, while their efficiency depends on not only the perfection degree of the heat-into-work conversion, but on also the intensity of the heat exchange between the working medium and the heat wells. Therefore the real cycle efficiency is always overestimated. This fact poses the problem of revealing the limiting capabilities of real processes considering not only the temperatures of heat wells, but also the heat transfer coefficients, duration of a cycle in whole and its particular stages, cycle-averaged power, etc. Curson and Ahlborn were the first who proposed such a problem definition (1975) having considered the conditions of developing a Carnot cycle providing the peak cycle-averaged power N at temperatures of heat well and heat sink of T_h and T_c, respectively. In this definition the working medium receives and releases heat at the constant temperatures $T_1 < T_h$ and $T_2 > T_c$. (Curson, Ahlborn, 1975). The optimal values of these temperatures are to be found here corresponding to the cycle peak power at a contact duration between the working medium and the heat well and heat sink of t_h and t_c, respectively, when the heat flows in-between them obey a linear law of the type:

$$J_q' = L_h (T_h - T_1) \; ; \quad J_q'' = L_c (T_2 - T_c) \, , \qquad (12.5.1)$$

where L_h , L_c – constant heat transfer coefficients.

Settling the values of the parameters t_h and t_c as satisfying the limitations $J_q'/T_1 + J_q''/T_2 = 0$ (ensuing from the entropy variation cyclic character) the authors express the power $N = (J_q''t_h + J_q''t_c)/t$ averaged thru the cycle duration $t_h + t_c = t$ as a function of above parameters and find the peak of this function allowing for the said limitations. In this case the thermal efficiency corresponding to the cycle peak power $N_{\max}$ is defined by the relation:

$$\eta_t^{opt} = 1 - \sqrt{T_c / T_h} \, . \qquad (12.5.2)$$

As can be seen, the optimal thermal efficiency of such a cycle is considerably lower than the ideal Carnot cycle efficiency at the specified values L_h, L_c of heat transfer coefficients and the peak power.

Many works dedicated to thermodynamics of finite-time processes are characteristic by the fact that they consider limitations of various kinds, viz. for working medium minimal and maximal volumes (Curson, 1975; Rubin, 1980), for piston acceleration in internal combustion engine (Band, Kafry, 1981), for heat amount Q_h received from a heat well (Rubin, 1979; Band, 1982), etc. A great number of works in this field are dedicated to investigation of systems where the heat flow from a heat well to the working medium is considered as given in the form of some time function $J_q(t)$ (Salamon, 1981; Fairen, 1982). It is worth noticing that the first overview of works dedicated to finite-time processes thermodynamics (Barrer, 1982) was published in France as early as in 1980. It is mentioned therein that taking the time factor into consideration when optimizing the cycles of heat engines allows estimating the efficiency of real plants relating their parameters to the limiting parameters of irreversible cycles having the same power, heat transfer coefficients, duration, etc. Thus the finite-time thermodynamics reveals the limiting capabilities of energy conversion irreversible processes in heat engines at finite duration of the heat application and abstraction processes (and, consequently, finite duration of the cycle), as well as under various limitations to the plant parameters. Its methods are starting to be successfully applied to estimate the efficiency of not heat engines only, but also processing plants, in particular, the photovoltaic cell-based plants and the plants of water decomposition into oxygen and hydrogen (Dung, 1982). Attempts are known to optimize by this method the chemical efficiency of tubular reactor (Ondrechem, 1980), as well as the output power of pulsating laser (Keren, 1982) and the installation using the radiant energy (Adler, 1981; Mozurkewich, 1983). Thus the application sphere of finite- time thermodynamics is rapidly widening (Linden, 1992). This is promoted by not only the need to clarify the limiting capabilities of thermodynamic processes. Posing the problem in this theory changes the efficiency criteria for heat engines and processing plants bringing them closer to reality. At the same time it is worth noticing that finite-time thermodynamics considers only the so-called externally irreversible cycles where the cycle-comprising processes themselves are considered equilibrium (internally reversible). Such inconsequence is explained by the fact that finite-time thermodynamics imports the transfer equations involving the process rate from outside, i.e. from the heat exchange theory. Process time and productivity do not now, as before, enter in the equations of finite-time thermodynamics which is thus incapable to describe the kinetics of the thermodynamic systems' transfer from some non-equilibrium state into another (i.e. the motion of such systems). Furthermore, this theory is based on solely the cycle method and is therefore inapplicable to the analysis of the heat energy direct conversion plants, as well as to the flow-type machines. Besides, it does not consider the kinetics of energy-conversion process itself and assumes that the duration of arbitrary cycle in finite-time thermodynamics is added of only the times of heat application and abstraction. In the absence of unanimous approaches to the energy dissipation in the energy transfer and conversion processes the circle of problems solvable by the methods of finite-time thermodynamics appears to be considerably limited. In this respect the synthesis of thermodynamics and economics – "thermo-economics" – offers a noticeable advantage. This direction in thermodynamics of the XXth century is aimed to commensuration of savings in fuel and material due to plant efficiency upgrade and the investments associated. At the same time it should be noted that the irreversibility of useful work processes in thermo-economics is also considered not on the basis of their kinetics study, but by introducing constant relative efficiencies of these processes, i.e. without the relationship between power and cost effectiveness of engineering systems taken into consideration. From here the problem ensues to directly introduce the factor of real process productivity (useful power) into the equations of thermodynamics as a thermodynamic variable along with the process time and rate. This problem has been solved in thermokinetics that does not exclude from the consideration the irreversible part of a real phenomenon (like in Thomson's pseudo-thermostatics) or its reversible part (like in Onsager's quasi-thermodynamics) and may be applied to investigation of processes with any degree of irreversibility.

As shown above, in search of conditions to reach the peak cycle power finite-time thermodynamics proceeds from the ideas usual for thermostatics about the possibility to vary the durations of heat application Δt_1 and abstraction Δt_2 processes in cycles and to include them in the number of the parameters being optimized (Curson, Ahlborn, 1975). In this case the optimal duration of contact between the working medium and the heat well and sink appears to be dependent on the heat transfer coefficients. However, these ideas appear to be invalid when considering a steady-state energy conversion process in a thermal power plant. As shown above, the availability of a "transit" (crossing the system invariable) flow of corresponding energy carrier is the necessary condition of useful work done. For heat engines this is expressed as the equality of total entropy flows entering and leaving the engine $J_s' = -J_s''$ (11.2.7). Comparing this condition with (11.2.6) and taking into consideration that for any cycle $\Delta S_1 = -\Delta S_2$ drives to a conclusion that the durations the working medium contacts with the heat well and heat sink are equal to each other:

$$\Delta t_1 = \Delta S_1 / J_s' = \Delta S_2 / J_s'' = \Delta t_2 . \qquad (12.5.3\ )$$

Thus, unlike finite-time thermodynamics, thermokinetics introduces the additional condition $\Delta t_1 = \Delta t_2$. This provides such a result that the temperatures of heat application T_1 and abstraction T_2 appear to be interrelated. To reveal this relationship, let us consider the identity of the mean thermodynamic heat application and abstraction temperatures T_1 and T_2 to the mean integral temperatures of the heat flow entering and leaving the plant T' and T'', which is ascertained in the previous chapter. This allows expressing the thermal efficiency of an arbitrary cycle in terms of the heat flow parameters:

$$\eta_t = 1 - \overline{T}_2 / \overline{T}_1 = 1 - T''/ T' = 1 - J_q''/J_q' . \qquad (12.5.4\ )$$

Representing on this basis the phenomenological laws of heat transfer between the heat well and heat sink with temperatures of T_h and T_c and the working medium in the cycle as:

$$T_h - T_1 = R_h J_q' \,;\ T_2 - T_c = R_c J_q'' \,. \qquad (12.5.5)$$

where R_h , R_c – overall thermal resistance to heat exchange from the heat well and heat sink, respectively, easily gives that the temperature drops from the heat well and heat sink are related with the thermal resistances thru the relationship:

$$(T_2 - T_c)/(T_h - T_1) = (1 - \eta_t)\, R_c/R_h. \qquad (12.5.6)$$

Expanding the expression of η_t a relationship between the temperatures of heat application and abstraction can be easily obtained (V. Etkin, 1991):

$$T_2 = T_1 T_c/[T_1(1 + R_c/R_h) - T_h R_c/R_h]. \qquad (12.5.7)$$

This relationship existing demands a correction of the conditions under which the peak cycle power can be obtained. Let us consider for example the problem of determining the optimal (at peak power conditions) heat application temperature in cycles of a nuclear power plant (NPP) on saturated steam (Calafati, 1963). Let the heat pick-up from a light-water nuclear reactor J_q' be restricted by the temperature T_{max} of the fuel elements. Then the theoretical power of the plant N_j defined as the product of the heat flow J_q' from the heat well by the thermal efficiency of the NPP cycle $\eta_t = 1 - T_2/T_1$, where T_1, T_2 – mean integral temperatures of heat application and abstraction, respectively, in the NPP cycle, will have a peak due to efficiency deterioration as the heat flow from the heat well J_q' increases. Let us assume after the work mentioned that the temperature averaged over the heat exchange surface is identical to the mean integral temperature T_1 of heat application to the working medium (so that $J_q' = (T_h - T_1)/R_h$, where T_h, R_h – mean integral temperature on the surface of the fuel elements and thermal resistance to the heat transfer from the heat well to the working medium, respectively). Let us also assume that the coefficient of heat release and temperature distribution variation over fuel element height $k_p = (T_h - T_1)/(T_{max} - T_1)$ does not depend on power. Then the NPP power will be:

$$N_j = J_q'\eta_t = k_p (T_{max} - T_1)(1 - T_2/T_1)/R_h \,. \qquad (12.5.8)$$

Considering this expression as a function of the initial cycle temperature T_1 and allowing for relation equation (12.5.7) after a number of transformations with constant T_h and T_c gives the optimal heat application and abstraction temperatures in peak power cycles (Etkin, 1997):

$$T_1^{\mathrm{opt}} = (\sqrt{\overline{T}_h \overline{T}_c} + T_h R_c/R_h)/(1 + R_c/R_h)\,, \qquad (12.5.9)$$

$$T_2^{\mathrm{opt}} = (T_c + \sqrt{\overline{T}_h \overline{T}_c}\; R_c/R_h)/(1 + R_c/R_h)\ . \qquad (12.5.10)$$

These expressions differ from those obtained in finite-time thermodynamics in the degree of the R_c/R_h contagion. It may be easily found that this ratio features the interrelation between the heat application and abstraction temperatures in an arbitrary cycle. In fact, considering T_2 as a function of T_1 and differentiating (12.5.10) under the R_c/R_h constancy with η_t^{opt} independent on this ratio gives:

$$\partial T_2/\partial T_1 = -R_c/R_h\,(1-\eta_t)\ . \qquad (12.5.11)$$

From this it follows that the relation degree between the heat application and abstraction temperatures T_1 and T_2 is defined by the R_c/R_h ratio. To illustrate how it is important to take into account the relation between initial and final parameters for the power plant optimization, let us consider a specific example of determining the optimal heat application and abstraction temperatures in NPP cycles with water-cooled reactors, for which, due to the minor c_T value, the peak power operating conditions are most economically advantageous (Calafati, 1963). However, unlike the traditional approach to determination of the NPP peak power cycle initial parameters based on the usual assumption of cycle heat abstraction temperature T_2 constancy, we will proceed from expression (12.5.11). In the calculations following the author mentioned the maximal temperature of the fuel elements made of metallic uranium is adopted as T_{max}= 928 K (650°C) and T_2=302 K, which according to (12.5.2) gives the value $T_1^{opt} = \sqrt{T_{\max}\overline{T}_2} = (928\cdot302)^{0,5}$ = 528 K. Like in the work mentioned, it is assumed in the calculations that the coefficient of temperature distribution variation over fuel element height with cosine heat release distribution $k_p = 2/\pi$ does not depend on power, which corresponds to the mean integral temperature of the fuel elements as the heat well T_h= 782.8 K. The results of such calculations for various R_c/R_h ratios are shown on Fig.12.4.

As follows from the figure, the optimal heat abstraction temperature considerably exceeds its usually adopted level already at enough low values of $R_c/R_h \approx 0.05...0.08$ typical for NPP. As the R_c/R_h ratio increases, the gap becomes especially noticeable. This fact evidences the necessity to jointly assign the initial and final cycle parameters of a power unit considering their relation. This interrelation becomes especially important for spacecraft power units where the heat abstraction into the ambient space is provided by radiation, while the R_c/R_h ratio increases by almost two orders. To confirm the said, let us consider a particular example of the American orbital station elaborated by General Electric (Favorsky and others, 1970). Its steam turbine power unit comprises a nuclear reactor with a thermal power of N_T = 8

MW, a steam turbine in complete with a generator with a net electric power of N_e = 1 MW and a finned-tube radiator cooler. The power unit features two main liquid-metal circuits. Liquid lithium is the working medium of the first circuit, while potassium – of the second one. The temperature of the potassium entering and leaving the turbine is 1,065^{0}C and 704.4^{0}C, respectively. The maximum allowable temperature of the fuel element is 1,221^{0}C and the temperature of the potassium entering and leaving the reactor is 1,037.8^{o}C and 1,093.3^{0}C, respectively, which corresponds to the mean integral heat application temperature thru cycle $\overline{T}_1 \approx 1{,}324$ K. The cycle thermal efficiency η_t corresponding to the heat abstraction temperature $\overline{T}_2$ = 977.5 K is equal to 0.26. The equilibrium temperature of the radiator cooler T_c (in the absence of Q_2) found from the heat balance between the solar radiation flow onto the radiator cooler surface and the heat abstraction from the radiator cooler into the ambient space by radiation is tentatively 750 K. At these conditions the R_c/R_h ratio found from expressions (12.5.6) is equal to 2.1–2.2, which exceeds by two orders its value usual for ground thermal power plants. Optimal heat application and abstraction temperatures found for these parameter values from (12.5.6)–(12.5.7) are $\overline{T}_1^{opt}$ = 1350 K and $\overline{T}_2^{opt}$ = 960 K, respectively – quite close to their true values. At the same time it is noticeable that the plant cycle heat abstraction temperature appears to be 210^{0}C higher than the conditional temperature of the sink. This stresses the necessity of interrelated search of optimal heat application and abstraction temperatures in the cycles of power units.

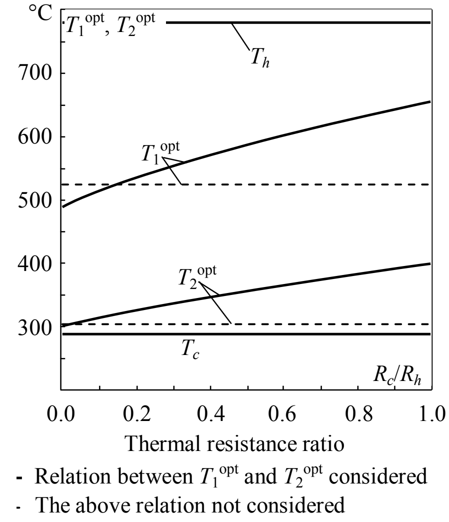


Fig.12.4. Interrelation between Heat Application and Heat Abstraction Temperatures in NPP Cycles with Water-Cooled Reactors

The examples considered herein evidence that thermokinetics substantially expands the applicability of finite-time thermodynamics allowing not only to extend its methods to systems with various value of optimal load, but also to clarify a number of its deductions.

Chapter 13

CONVERTERS OF FIELD FORMS OF ENERGY

> "…It is just a matter of time,
> how soon mankind will succeed in
> connecting its machines to the very
> power source of the ambient space"
> N. Tesla

Matter is known to exist in two forms, viz. substance and field. Up to date mankind have used the energy of only the former of them. Such are, in particular, the chemical energy of fuel and the nuclear energy of spontaneously fissionable elements. The final product of the substance energy conversion is in most cases a substance in its modified state, which is accumulated on the planet directly endangering its ecological stability. The problem is aggravated by the concentration of population within huge megapolises and by increasing consumption of energy resources. The energy generation has become increasingly centralized, hydropower dams and thermal power plants have become increasingly gigantic, oil and gas pipelines, as well as power transmission and heat supply lines – increasingly extended. This just facilitates an ecology crisis and aggravates the consequences of natural disasters. Fossil fuel resources are being depleted, while the share of renewable energy sources remains extremely low. In search of new energy sources the scientific community takes the ever growing risk postponing for an uncertain time the solution of the problem of nuclear waste disposal and conservation of the exhausted nuclear plants. Vast funds are being spent to harness the thermonuclear reactions. It seems as though there is no a way out of the situation.

Meantime, in the present circumstances mankind ought to pay closer attention to such alternative forms of renewable energy as the energy of the field forces surrounding us.

13.1. Theoretical Possibilities of Creating Alternators

According to information received to date there are more than couple of tens of devices in operation with an output exceeding the measurable input, and more than a hundred of patents granted for such devices in different countries. Such devices are often called the "free energy generators", "overunity devices" (with efficiency in excess of 100%), "surplus power generators” and even “perpetual motion machines”. The authors of such publications are not willing for various reasons to recognize the energy sources not estimable by present-day means. It comes down even to the fact that the ambient energy consumption is neglected just due to the absence of…the tangible costs associated. This can not be justified by whatever considerations, the more so because all renewable energy sources feature low expenses.

Since the physical content of these terms absolutely violates energy conservation, it should be rather construed that such devices would use unaccounted energy sources alternative to not only conventional organic and nuclear fuels, but also to renewable energy sources. Therefore they will hereafter be termed *alternators* 1) for short. However, the authors of publications for various reasons do not wish to recognize as energy sources those inestimable by modern means. It comes down to even disregarding the energy from unknown sources because of unavailability… of the tangible costs associated.

At these conditions it looks like reasonable that alternators be analyzed via application of thermokinetics which body of mathematics, unlike the cycle method of classic thermodynamics, operates exclusively parameters of energy converting system itself rather than energy (heat) sources. It is just apropos for alternators since the energy sources and their streams, as well as their parameters, remain unknown in most cases.

According to thermokinetics, for thermodynamic analysis of an arbitrary machine converting some i^{th} field form of energy into the j^{th} form, the law of energy conservation (2.3.9) should be used, which for the case of vector forces acting gives:

$$dU = \text{đ}Q^{\text{д}} - \mathbf{X}_i \cdot d\mathbf{Z}_i - \mathbf{X}_j \cdot d\mathbf{Z}_j = 0. \qquad (13.1.1\ )$$

This equation differs from the Gibbs’ generalized relationship the classic thermodynamics operates since it does not contain the terms $\Sigma_i \psi_i d\Theta_i$ describing transfer of the energy carrier Θ_{i} across the system borders and, on the contrary, contains the term $\text{đ}W_j = \mathbf{X}_{\mathrm{j}} \cdot \mathrm{d}\mathbf{Z}_j$ describing the work done by the force field and working medium itself. In the particular case of electrical and magnetic fields the parameters $\mathbf{X}_i$ and $\mathbf{Z}_i$ refer to the working medium, while the parameters $\mathbf{X}_j$ and $\mathbf{Z}_j$ – to the object the work applies to. The terms $\mathbf{X}_i \cdot \mathrm{d}\mathbf{Z}_i < 0$ and $\mathbf{X}_j \cdot \mathrm{d}\mathbf{Z}_j > 0$ characterize here, respectively, the work done on the working medium by the force field and the work done by the working medium itself on the object the work applies to; the term $\text{đ}Q^{\mathrm{d}}$ describes the

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1) The term “alternators” refer presently to the only class of the “over-unity devices”, viz. magnetic motors and generators. We will refer to it in the wider sense.

elementary dissipation heat released for the time t within the system volume V. As can be seen, to analyze the cycle involving a non-equilibrium working medium, there is no need to know the parameters of the energy source. This makes it possible to analyze the processes running in energy converter without knowing the parameters of the energy source. Such an analysis, as shown in Chapters 13 and 14, includes finding the motive forces $\mathbf{X}_i$, $\mathbf{X}_j$ and the energy carrier flows $\mathbf{J}_i$, $\mathbf{J}_j$ for energy forms being and having been converted, formulating the laws of energy conversion (11.4.1–11.4.2) in a particular machine, finding the similarity criteria (11.4.6–11.4.7), determining the power efficiency of the machine and revealing the deviation of its operation from optimum for this particular type of energy converters. These problems outstep the classic theory of heat engines.

Unfortunately, such an analysis does not give a unique indication of energy source. However, as shown in Chapter 14, with regard to renewable energy sources for which investments do not noticeably contribute to the net cost of the energy generated, their consumption is not of fundamental importance. Therefore the alternators are to be considered as ranked with other machines operating on renewable energy sources. However, the fact should not be left out of consideration that a field form of energy, from the positions of thermokinetics, is caused by heterogeneous distribution of "field-forming" material objects in space and, therefore, belongs to them, but not to space itself (ether or physical vacuum), whatever properties we may try to attribute to this space. It remains to show that whatever "free energy generation", "surplus power" and "over-unity efficiency" are out of the question. To do so, the equation (15.1.1) is easier to be represented in the form of the energy balance equation

$$dU/dt = N_i - N_j - N^d. \qquad (13.1.2)$$

Here N_i means the power input to the alternator; N_j – net power of the device; N^d – dissipation power in the system. From here the power efficiency expression ensues, which for cyclic machines (dU/dt = 0) according to (11.2.9) takes the form:

$$\eta_N = N_j / N_i = 1 - N^d/N_i \le 1 \ . \qquad (13.1.3)$$

Thus the efficiency of any real energy converter (with $N^d/N_i > 0$) is always below unity, i.e. the work of alternators is always done in strict compliance with the laws of thermodynamics and without violation of its first law.

It should be also clearly understood that using a field form of energy in order to convert it into other (more convenient for user) forms is possible inasmuch as it is ordered. Let us now show that a field form of energy meets this requirement, too, despite the known expression for the wave energy U_w valid for waves of any character (acoustic, hydraulic, electromagnetic) and not containing vector parameters:

$$U_w = \rho A_w{}^2\omega^2/2\ . \qquad (13.1.4)$$

Here ρ – oscillating medium density; A_w – oscillation amplitude; ω – oscillation angular frequency.

Let us show that any wave with an amplitude of A as a bilateral deviation of the oscillating value Θ_w from its equilibrium value is characterized by some distribution moment $\mathbf{Z}_w$. To do so, we have to consider a stretch out of an arbitrary wave sequence with the oscillating value monotone increasing or decreasing (in our case, the density ρ_w of the parameter Θ_w (Fig. 13.1)).

In this figure the crosshatched regions feature the part $\Theta_w{}^*$ of the value Θ_w transferred from some domain of space into another. As a result, the centers of the value $\Theta_w{}^*$ for each quarter-wave part λ/4 shift from the positions $\mathbf{r}_\mathrm{o}'$ and $\mathbf{r}_\mathrm{o}''$ they would occupy at uniform distribution of ρ_w for quarter-period to the positions $\mathbf{r}'$ and $\mathbf{r}''$. The distribution moment $\mathbf{Z}_w$ is defined in this case by the same expression (1.5.7), but with the elements $d\Theta_i$ replaced by $\Theta_w{}^*$:

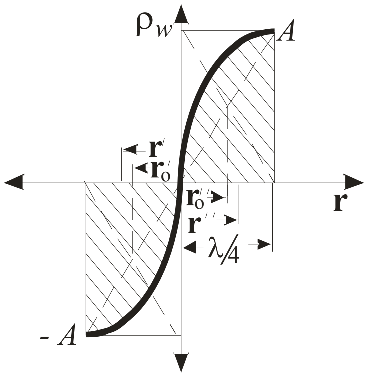

Fig.13.1. To distribution moment generating in single wave

$$\mathbf{Z}_w = \mathbf{r}'\Theta_w{}^{*\prime} + \mathbf{r}''\Theta_w{}^{*\prime\prime}. \qquad (13.1.5)$$

Since $\Theta_w{}^{*\prime} = -\Theta_w{}^{*\prime\prime}$, expression (13.1.5) may be represented in the same form as the dipole moment:

$$\mathbf{Z}_w = \Theta_w{}^*\Delta\mathbf{r}\ , \qquad (13.1.6)$$

where $\Delta\mathbf{r} = \mathbf{r}'' - \mathbf{r}'$ means the dipole moment arm. It is significant that, like in the case of dipole, the terms of (15.1.5) are not mutually neutralized, but summarized since the signs of $(\mathbf{r}' - \mathbf{r}'_\mathrm{o})$, $(\mathbf{r}'' - \mathbf{r}''_\mathrm{o})$ are opposite like for $\Theta_w{}^{*\prime}$, $\Theta_w{}^{*\prime\prime}$. Thus the oscillation of whatever medium may be considered as a kind of its polarization. This allows finding the motive force $\mathbf{X}_w$ to the process of radiant energy exchange by the same way, i.e. as the derivative of the wave energy U_w with respect to the distribution moment $\mathbf{Z}_w$, i.e. $\mathbf{X}_w = -(\partial U_w/\partial \mathbf{Z}_w)$. However, in this case it is even easier to use expression (2.5.2) giving:

$$dU_w = -\Theta_w d\psi_w = -\rho A\omega\ dA\omega, \qquad (13.1.7)$$

From this it directly follows that the “wave potential” is equal to the product of amplitude and wave frequency: $\psi_w = A\omega$, while the motive force of oscillation energy exchange $\mathbf{X}_w = -\nabla A\omega$, i.e. is expressed in terms of negative gradient of this potential which we will hereinafter refer to as “amplitude-frequency”. As can be seen, this type of energy exchange is in the general case directed toward equalizing amplitudes and wavelengths. It occurs with a disturbance of matter–field equilibrium, which manifests itself in any disturbance of amplitude balance or in frequency shift between external and natural oscillation processes. This refers, in particular, to radiant energy exchange which, according to existing concepts, features the electromagnetic character. This energy exchange is by no means reducible to heat exchange that occupies merely a minor part in the spectrum of electromagnetic oscillation with a wavelength λ of 0.4 to 4 μm 1)1) and has its own motive force defined for absolute black bodies by the difference between the forth powers of absolute temperatures.

The energy exchange arising between matter and field explains the functioning of alternators without recourse to whatever hypotheses and postulates lying beyond the existing scientific paradigm. Such a position basically differs from the opinion common for both the traditional academic ambience and alternative scientific forums which declare that, to substantiate the principle of operation and to develop the “over-unity” devices (with efficiency > 1), some novel “exotic” branch of physics is needed.

The further thermokinetic analysis of the alternators is advisably to be conducted in application to a particular type of working medium that provides the energy conversion in some of the stationary force fields. Hereafter we will consider examples of the energy converters for the force fields known, viz. gravitational, electrostatic and electromagnetic. Such a consideration is basically aimed at demonstrating the fact that the alternators follow the unitary thermokinetic laws of energy conversion.

13.2. Gravitational energy Converters

The idea to create the “perpetuum mobile” (perpetual motion) technical devices is rooted in philosophy of the Ancient Orient. This is the place wherein the first documentary evidences about the creation of a gravitation-based engine originate. Such is, in particular, the Bakhaskar “self-rotating wheel” (India) with tubes tangentially arranged and half-filled with water, which demonstrated in mid 12th century. In Europe the first projects of such

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1) Photosynthesis, photo-effect, photo-ionization, photoluminescence, photo-acoustic phenomena, photonuclear reactions, etc, involving radiant energy exchange – all those are evidence of the fact.

mechanical "perpetual motion machines" appeared in the 13th century: the V. Honnecourt's wheel with seven weights (France, 1245), the similar V. Maricourt's wheel (France, 1269). Leonardo da Vinci left a number of drawings behind him with a device where vertically falling weights or water rotated a wheel and thus worked efficiently. Mariano di Jacopo built in Italy (1438) a system of eight rods radially arranged in the plane of rotation and all bendable in one direction. Due to this fact the left half of the system differs from its right half in weight, thus, providing the rotation. Cornelius Drebbel, alchemist and magician, created a perpetuum mobile in 1610 (presumably). Robert Fludd had developed a plenty of devices of such a type up to 1630. Later on in 1870 many people tried to obtain patents for Fludd's device variations. Ulrich von Carnach developed a "ball" perpetuum mobile in Germany in 1664. The famous scientist Jean Bernoully (1667-1748) put forward a fluid-energy device project. Bockler designed a "self-rotating" mill in 1686 based on the Archimedes' screw in various versions.

In England the first perpetuum mobile patent was granted in 1635 for the E. Somerset's 4-meter wheel with 14 weights per 25 kg each. The machine was brilliantly tested in London in the presence of King Charles with a record available in the archives. One of such wheels E. Somerset demonstrated to the King of France in 1638. It is significant that already 600 patents for such devices had been granted in England up to 1903.

The wheel of J. Bessler (better known as Orffyreus) gained the most distinction in the early 18th century. For several tens of years he publicly demonstrated various models of his wheel set in motion with weights inside it, which developed an asymmetrical moment at wheel rotation. The last of his designs was 6 feet in diameter, 12 inches in thickness and rotated with a speed of 42 rpm. That wheel not only kept continuous rotation, but also allowed to do useful work, e.g. lifted a weight with a mass of 16 kg to a height of 1.5 m. Its operation was more than once scrutinized by famous scientists and officials, while German Prince Karl let into its design granted Orffyreus a certificate for "Perpetuum Mobile". Under control of a competent commission of 11 members (Professor Gravesaint, Newton's intimate friend, among them) the wheel kept working in a room locked and sealed up for 40 days and at a sudden inspection showed as-before rotation with a speed of 26 rpm. The tests repeated many times since the commission scrutinized the availability of secret drives (the reason wherefore the wheel changed its location).

As one can see, those were not charlatans at all who were occupied with perpetual motion machines. Therefore, it is hardly to credit of the Parisian Academy of Sciences, one of the highest authority at that time, that it resolved in 1775 (i.e. before the energy conservation law discovered) to exclude such projects from consideration. It is not out of place to note that still earlier that Academy had refused to consider the existence of meteorites as an absurdity of rockfall down from the heavens. It is well known what a confusion it caused. It is quite possible that if the French academicians had not disregarded a careful and unbiased consideration of such machines, power engineering and science in whole could have followed quite other path in their development. However, in reality an absolutely opposite situation developed: when an operating machine pretending to be the "perpetuum mobile" was publicly demonstrated, no reasonable refutations followed, but usually the case closed, as for the Orffyreus' wheel, with a magazine pamphlet.

Assuming that the task of real science is not at all the devotion to a paradigm having become antiquated long ago, let us consider, from the positions of thermokinetics, the operation of one of such devices, e.g. the Fraga's wheel (Cuba, USA Patent IL60915,1987).

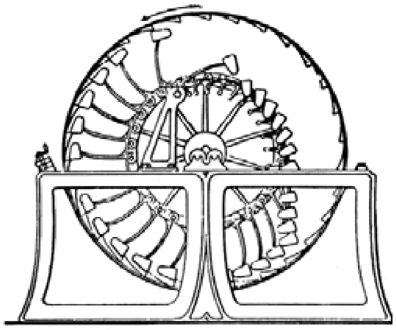

Fig. 13.2. Fraga's Wheel

This device constitutes a self-rotating wheel with non-balanced weights secured at the ends of levers (Fig. 13.2). The opposite ends of the levers accommodate movable joints enabling the levers to "tilt" when transiting the unstable equilibrium point. The wheel has a number of cogs securing the weights with the levers till the position of the maximum possible torque (left part of the wheel). On the contrary, the weights in the right part of the wheel are always in the position of the minimum possible torque. The device is induced to stable rotation by a minor push. For our case the basic equation of thermokinetics (2.2.5) has the form:

$$dU = TdS + \mathbf{F}_{\mathrm{g}} \cdot d\mathbf{R}_{\mathrm{g}} + \mathbf{M} \cdot d\boldsymbol{\varphi}\,, \tag{13.2.1}$$

where $TdS = \text{đ}Q + \text{đ}Q^{\text{д}}$ – total heat the system receives from outside ($\text{đ}Q$) and releases due to friction ($\text{đ}Q^{\text{д}}$); $\mathbf{F}_{\mathrm{g}}$ – gravity force; $\mathbf{R}_{\mathrm{g}}$– center-of-mass radius vector of the wheel; $\mathbf{M}=\mathbf{F}_{\mathrm{g}} \times \mathbf{R}_{\mathrm{g}}$ – torque applied to the wheel from gravitational field; $\boldsymbol{\varphi}$ – angle of wheel rotation.

Comparing this expression with the combined equation for the first and second laws of classic thermodynamics (2.2.7) wherein the expansion work pdV is superseded by other (the j^{th}) kinds of work $\text{đ}W_j$

$$dU = TdS - \text{đ}W_j\,, \tag{13.2.2}$$

gives that, should a heterogeneous system have the internal energy of gravitational interaction between system parts, the term $\text{đ}W_j$ includes the weight displacement work $\mathbf{F}_{\mathrm{g}} \cdot d\mathbf{R}_{\mathrm{g}}$ and the wheel rotation work $\mathbf{M} \cdot d\boldsymbol{\varphi}$.

Let us apply this equation to the circular process the Fraga's wheel runs:

$$\oint dU = \oint TdS + \oint \mathbf{F}_g\cdot d\mathbf{R}_g + \oint \mathbf{M}\cdot d\boldsymbol{\varphi} . \qquad (13.2.3)$$

This expression can be essentially simplified given the circuital integral of any state function, including system energy, equal to zero ($\oint dU = 0$) and the friction and external heat exchange neglected ($\oint TdS = 0$). Furthermore, since the gravity force $\mathbf{F}_g$ remains essentially invariable in circular process, then factoring $\mathbf{F}_g$ outside the integral sign and given $\oint d\mathbf{R}_g = 0$ gives that the second term on the right-hand side also becomes zero. Thus, from the positions of Newton's mechanics not catering for rotational motion (in the absence of the term $\oint \mathbf{M}\cdot d\boldsymbol{\varphi}$), the Fraga's wheel should be attributed to the "perpetual motion of the first kind". However, considering the third term on the right-hand side of (13.1.3) gives immediately that the Fraga's wheel cycle work $W_c = \oint đW_j$ is equal to

$$W_{ц} = \oint \mathbf{M}_g\cdot d\boldsymbol{\varphi}_g . \qquad (13.2.4)$$

This expression shows that the cycle work of gravitational converter may differ from zero if gravitational field does work for rotation of the wheel. This work may differ from zero since the field of torques is not potential. Let us now clarify the conditions making this work other than zero. To do so, divide circuital integral (13.1.4) into parts 1–2 and 2–1 wherein the angle φ varies from 0 up to 180^0 and from 180^0 down to 0. For the sake of simplicity represent the integrand (13.1.4) in terms of scalar values of M and φ_g and denote the torque and rotation angle for these parts of the cycle with single or double stroke, respectively (M', φ' and M'', φ''). Then based on (13.1.4) and given the opposite signs for the torques on these parts ($M'' = -M'$) one may write down instead of (13.1.4):

$$W_{ц} = \int_1^2 \left(M' - M''\right)\cdot d\varphi_g' \ . \qquad (13.2.5)$$

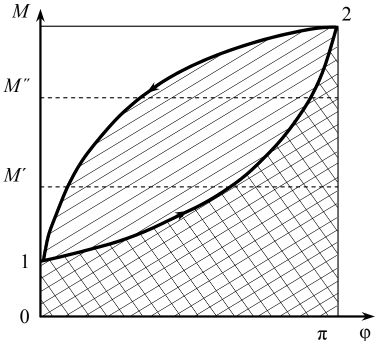

Fig. 13. 3. Cycle of Unbalanced Wheel in Gravity Field

The M–φ_g cycle of such a device for one of the weighted levers is plotted in Fig. 13.3. Let us assume that at initial time this weight takes the extremely lowest position (angle φ makes

0^0 to vertical). With an external force applied let us turn the wheel counterclockwise at an angle of 180^0 so that the weight arm R_g' remains minimal (process 1–2). This action is associated with an external work exerted and expressed by the cross-hatched area. With the apex position reached a weight "throw-over" will occur and the further rotation of the wheel will proceed as a self-motion (process 2–1). The self-motion work expressed by the hatched area under curve 2–1 will exceed the exerted work due to increasing R_g'' and the corresponding average torque M''. The weight lift along 1–2 will further continue without an exerting interference since the average counter-torque M'' will be lower. This is the principle of operation of the self-rotating wheels which do not thus violate whatever laws of physics and are not the "perpetual motion" in the common sense of this term. It remains only to show that the operation of such a device follows the same universal load curves as the other engines. In our case the forces $\mathbf{X}_i$ and $\mathbf{X}_{io}$ are construed as the moments $\mathbf{M} = \mathbf{g}R_g$, so the load criterion take the form $B = 1 - R_g'/R_g'' < 1$. As for the Q-factor Φ, it remains unknown. However, given the wheel friction, it is certainly below infinity, so from the curve in Fig. 14-2 it follows that the power efficiency η_N and the engine power N become zero at the balance of arms $R_g' = R_g''$ which is in strict compliance with experiment. From this it also follows that the device should be tuned to find the optimal relation R_g'/R_g''– the fact as well noted by the inventors of these devices. It remains only just to instantiate the above with several present-day designs of such devices. One of the most impressive machines of such a kind is the device (Fig. 13.4) A Kosta built (Patent France No95/12421, 1995). His 18-meter unbalanced wheel is the best wordless evidence of the inventor's earnest approach and confidence in integrity of the design he has created. This wheel operates to the same principle and contains 236 movable elements providing its rotation. It can rotate both clockwise and counterclockwise. As the inventor notes, the main problem of its fabrication was to reach the variation of the mass positions "in proper place and at proper time".

Fig. 13.4. A. Kosta's Wheel

In 2006 the power company Environ announced its readiness to bring to the market a generator SPEGG producing electric power without fuel consumption. The generator is a self-rotating wheel Warranlinc that is coupled to a current generator and has 16 spokes. Eight of them contain weights being in translation movement and thereby compressing springs. The wheel is designed so that it is always heavier on one side. This disturbs its equilibrium in gravity field forcing it to rotate. Thus the great idea to use inexhaustible "living forces" of nature is starting to take real shape.

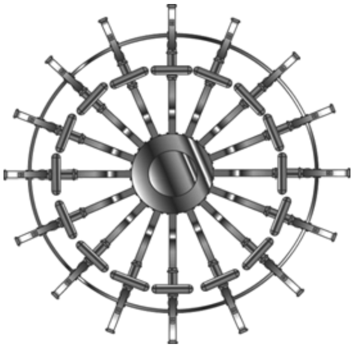

Fig. 13.5. Warannlinc Wheel

13.3. Generators Using Electrical Field energy

Let us now consider the generators using the energy of the natural electrostatic field. The Earth and its ionosphere are known to constitute a "spherical condenser" which energy content according to recent calculations (E. Rauscher, 2002) is about $3{\cdot}10^9$ kWh with a capacity of $15{\cdot}10^3$ μF. The intensity of the electrostatic field it generates averages 100 V/m. This gives hope to mankind, according to N. Tesla, "to connect its machines to the very power source of the ambient space". One of the possible designs he offered looks like an antenna in the form of a metalized balloon lifted above the ground and serving as an electric charge integrator. Being connected to an energy converter through a cable, this integrator is capable to use the "gratis" energy of atmospheric electricity. J. Swenson has conducted a series of simple experiments aimed at "energy recovery from air". Natural electrical oscillation frequency of the planet, as known yet from Tesla's time, is 7.5Hz. Swenson dealt with a resonance frequency of 375 kHz and a 10-meter antenna (Fig. 13.6). This version of the energy recovery from the ambient space has been implemented in the Efimenko's electrostatic generator described in the book "Electrostatic Motor" (1973). A cylindrical rotor rotates in the potential electrical field generating a power of about 70W by means of a usual dynamo. The electrical field of the Earth

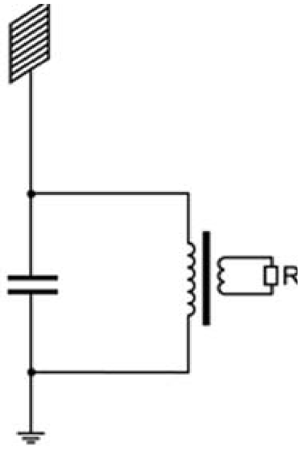

Fig. 13.6. Swenson's Generator Schematic

serves as a field source (6,000W), for which reason the machine has an antenna and grounding. Such machines using the potential difference between the planet surface and ionosphere have been known yet from 1800's. In this case not just posing a problem, but its solution is of interest.

In a number of cases the electrostatic fields can be generated artificially, which has been proven by the energy generator Testatica invented by P. Bauman and built in the Methernita Christian community. Several of such fuel-free generators have produced for 30 years an electric power of 750kW covering the entire community's demands (including also the workshops located in the same place). From the technical standpoint this device is the Wimshurst modernized influence machine. The machine features two discs with steel or aluminum segments fixed to the discs. The separation of the charges on the disc segments occur due to the brush friction. The brushes also pick up the charges on the disc segments. The self-rotation of the discs is provided by, evidently, the mutual repulsion of the wheel segments rotating in the opposite directions due to delay of the electrostatic interaction forces. The reaction force in this design can decrease by the relative displacement of the brushes assuring decreasing the charge on the segments at the moment the segments are drawing together. Such a machine with a disc diameter of 20 cm generates a power of about 200W; the large-scale machine has discs with a diameter of 2 m and generates about 30kW of power. A special diode module and Leyden jars provide frequency regulation. The design also includes permanent horseshoe magnets with coils connected to the Leyden jars and intended to maintain the frequency due to resonance, as well as a device stepping the voltage from 100kV (and more) down to 200V. Using permanent horseshoe magnets in the modern converter version is noted to considerably increase EMF.

In this aspect it is much more promising to use "electrodynamic" effects associated with the pulsed operation of devices using natural electricity. Yet N. Tesla, when conducted experiments with high-voltage DC generator, spark discharger and high-voltage air-core transformer (Tesla transformer) in the ninetieth of the 19th century, noticed a considerable increase in the power the device released into the environment against the high-frequency AC generator with a conventional step-up transformer. Tesla called that power increment "radiant electricity" having attributed it to ether and opposed to the conventional electric current as an electron stream. That statement was based on the effect Tesla discovered, which generated a voltage spatially distributed. The latter grew along the secondary coil length of his non-electromagnetic transformer and might thousands times exceed the spark discharger initial voltage and not to be proportional to the number of ampere-turns (since there was no current in the winding). That "electro-radiant" effect appeared when the high-voltage direct current was discharging to spark gap and broke before the back (reverse) current appeared. The effect intensified with a capacitor included in the high-voltage DC power supply. The energy flux caused by that effect spread in the form of a longitudinal electrostatic "light-like" beam that moved perpendicularly to the coil turns like incompressible gas under pressure and did not penetrate into the conductor. Fast interruption of direct current with magnetic interrupters generated a shock wave in the laboratory wherein the Tesla transformer was installed. This wave might be sensed as a sharp shock and an electric discomfort ("tickle") that, unlike the conventional electromagnetic radiation, penetrated through metal shields and most of dielectrics. Nevertheless, the pulses the Tesla transformer radiated, when shorter than 100 microseconds, were absolutely harmless to people and did not cause heating. The magnitude of those pulses depended on their duration and on the spark discharger voltage. They generated light effects in the vacuum tubes and caused a "response" in metals in the form of electric charge accumulation.

Thomas Henry Moray (USA) was among the Tesla's followers. In 1909–1910 he created a number of devices operating, as he believed, on electrostatic charge of the Earth and ionosphere. One of such demonstrational devices was represented to experts for review (with the exception of a small box that the author preferred having kept in his breast pocket). The device consisted of capacitors, step-up transformer, spark discharger and a panel with two radio tubes, as well as of a permanent magnet, switchers and lamps of 100W and 20W as a load. Whatever batteries were absent in the device, however, the design included antennas with a length of up to 200 feet elevated about 80 feet and a grounding deepened about 7 feet. The device was tested for a time period lengthy enough at both home conditions and in the mountains (far from power transmission lines). Some of the devices developed a load power of up to 650W at a voltage of up to 250kV. As can be seen, there are many elements in this device similar to the Tesla's technique.

Many of such elements can be revealed in the "over-unity" engine-generator of Edwin Grey (USA). For a period of 1961–1986 he built and patented several prototypes of self-sustained EMA devices (Electric Magnetic Association) capable to generate electric power without fuel used and to supply the needs of an apartment house, automobile, train or plane. Repeated demos of his technique gained enthusiastic comments in the press, while Grey himself was honored with a title of "Inventor of the Year" (1979) and with the "Quality Certificate" from R. Reagan, who was the Governor of California at that time. Like the Tesla's device, the Grey's generator was powered with high-voltage direct current. However, instead of the high-voltage DC generator, a battery was used there with the output interrupted through a multi-vibrator. The pulses from the multi-vibrator were delivered to the primary coil of a conventional transformer with the high-voltage winding connected to a bridge-type rectifier. Like in the Tesla's device, the high-voltage DC power supply periodically charged a high-value capacitor. The spark discharger was one more mutual component. However, instead of the transformer, the Grey's device used an "electrical conversion switching element tube" which consisted of a resistor, spark discharger and "charge receiving plates", i.e. combined three components of the Tesla's device. It was the electrical conversion switching element tube that did work when powered an engine, TV set, radio set, incandescent-filament lamps, etc. The "cold electricity" circuit, as Grey called it, operated likely in the following way: the storage battery voltage was stepped up to 3,000 V and stored in a high-value capacitor. Then the pulses discharged through a spark gap governed by electronic tubes so that the pulse duration was less than 50 microseconds. That intermittent pulse sequence passed through the conversion switching element tube where was entrapped on the charge receiving plates. The load was provided as a transformer that stepped the voltage down to power the electronic tubes and other loads, as well as an additional step-down transformer to charge a secondary battery. Having the batteries periodically switched, Grey not only recovered the power supplied, but also received an imposing "surplus" power. Nevertheless, all his attempts to apply his technique for commercial purposes failed. In the late 1970th the company Zetec, Inc. bought up the Grey's technology, while the inventor's attempts to intrigue the US Government and Senate in his work were not responded. Edwin Vincent Grey died in April 1989 in his workshop in Sparks (Nevada) at the age of 64 under the mysterious circumstances.

However, ideas never die without leaving a trace, which is once again confirmed by the Testatika energy generator invented by Paul Baumann and built in the Methernita Christian community (Switzerland). Several of such fuel-free generators have produced for 30 years an electric power of 750 kW covering the entire community's demands (including also the workshops located in the same place). Like in the case of E. Grey, the idea was suggested to P. Baumann through studying lightning. Unlike Tesla and Grey, to obtain a high-voltage DC source, the Wimshurst (1832–1903) generator was used, which application was practically ceased with electromagnetic generators introduced. The Wimshurst generator consisted of two discs which rotated in the opposite directions and had steel or aluminum segments fixed to them. The separation of the charges on the disc segments occurred due to the brush friction. The brushes also picked up the charge on the disc segments. The charge then drained into the Leyden jars and stored there. In the Testatika (see Fig. 13.7) the high voltage from these capacitors is supplied to the top of large metallic jars (which contents P. Baumann never showed to anyone and which caused a lot of guess-work – from

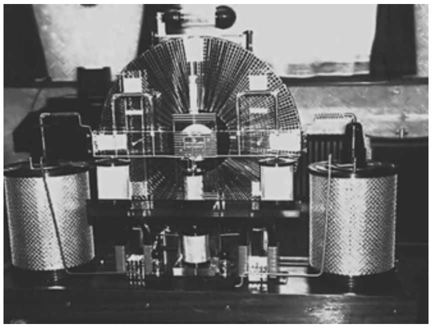
Fig. 13.7. Testatica Generator

capacitors with uranium additives and to a fancy crystals–magnets combination) and then removed out of the bottom to spark dischargers. In the figure two permanent horseshoe magnets can be seen along with the spark dischargers. Thus the Baumann's generator uses the same elements to enhance spark formation and arc breaking as in the Tesla's machine.

The self-rotation of the discs after an initial impact is provided by the mutual repulsion of the segments in two wheels due to the forces of electromagnetic interaction since the rotating electrified disc of the generator forms together with the external circuit a high current loop where the current runs in the discs in the opposite directions. Electrostatic repulsive forces may also take part in the process. The rotation is adjusted by a relative displacement of the brushes. A prototype of such a machine with a disc diameter of 20 cm generated a power of about 200 W. The large-scale Testatika machines have discs with a diameter of 2 m and generate about 30 kW of power. A special diode module and the Leyden jars provide frequency regulation. The design also includes a device stepping the voltage from 100 kV (and more) down to 200 V.

The fact the machine exists and operates is confirmed by the reports available from 12 recognized scientists who visited the community at different times to investigate and check the Testatika integrity (including Prof S. Marinov, who built working models of the generator and finally perished under the mysterious circumstances). All of these reports come to the recognition of the fact that the principles of Testatika's operation remain obscure.

The William Hyde's device (Patent USA No4897592, 1987) is one of the operating up-to-date designs close to the Baumann's machine in its technical solution. The author called it a "system generating power from electric field". It includes conventional elements of an electrostatic generator using rotating discs with segments like in the Swiss M-L converter Testatika. In the prototype of 1987 Hyde used up to 240 rotor segments and 480 stator segments. His generator rotates with a speed by an order of magnitude exceeding the Testatik speed. Furthermore, Hyde supplemented his design with several new elements, viz. stator discs on electrode plates, external 3 kV-power supply charging these electrode plates, etc. With such a potential the pulse voltage on the stator reaches 300 kV. The double rotor discs in his machine rotate in the same direction. Due to this fact the paired stator segments appear to be periodically screened against the polarizing effect of the exciter. Each stator segment in the machine is electrically coupled with its pair through a circuit where the pulse voltage is reduced and rectifies for the output circuit. To accelerate the machine rotor, Hyde uses the potential electrostatic field on that path of the process where the field work is positive. Where the field decelerates the rotor, Hyde partially shields it. So an unbalance of the forces $\mathbf{F}_i'$ and $\mathbf{F}_i''$ is created demanded by thermokinetics and allowing to obtain the energy from the stationary field source. The generator output is 22.9 kW with an input of 2.4 kW and a total load power of 20.5 kW. Due to its features, as well as to its description available, the self-rotating electrostatic Hyde's generator is one of the most attractive alternator designs.

One of the recent domestic designs is worthy of notice – the hydromagnetic dynamo by O. Gritskevich – patented yet in 1988 in the USSR as a "method of generation and electrostatic plasma generator as its embodiment". Considering our planet as a huge electrostatic generator the inventor offered a method to convert the force field of the planet into useful energy. The method was based on known physical principles, but used unique design solutions. The "non-mechanical" dynamo by Gritskevich was configured as doughnut-shaped bread roll with water as the rotor. Those generators agnominated as "water-warmers" had no pumps and none of the rubbing parts. They were operable for years practically without maintenance and not consuming even a gram of fuel. At the same time they were compact to be accommodated in any house and even a car. The cost of energy they generated was fortyfold lower than by a nuclear power plant, twentyfold lower than by a thermal power plant and fourfold lower than by a wind motor. The first prototype successfully operated in the mountains of Armenia and supplied the on-site needs of a scientific research station. However, despite the Rospatent certification and approval of scientific community, the hydromagnetic dynamo by Gritskevich has not found the market demand neither in Russia nor in the USA, where the inventor and seven of his mates from the design bureau emigrated in the late 1999. This circumstance evidences ones again that the main point here is not only the scientific consistency of the alternators pertaining to this class and even not the search of their most promising design solutions, but the geopolitics of the energy park holders.

13.4. Current Generators Using Magnetic Field energy

The current generators based on permanent magnets constitute the most numerous and diversified class among the devices attributed to the "perpetual motion" category. The capability of the permanent magnets to do useful work (e.g. to lift metallic objects) has been known since several centuries ago. Since that time enthusiastic individualists have endeavored to use them. Yet seven centuries ago P Piligrim offered the first magnetic engine. In the 16th century Jesuit priest J. Taisnerius was possessed with idea to create a magnetic "perpetuum mobile". Later on the number of such projects rose to an avalanche and to date has reached such a scale that it becomes possible to introduce a branched classification of such devices by various criteria. The specific category of USA patents granted under the presentation of an acting model of the device claimed is the official confirmation of the integrity of some of the devices. Therefore, it is a matter of interest to demonstrate that the alternators of this class do not either violate whatever laws of thermokinetics and are attributed to the "over-unity" devices just through misunderstanding.

The magnetism of substances is known to be caused by basically the orbital motion of electrons, as well by their spin magnetic moments. Each of the magnets has its own "magnetic ordered energy" content, i.e. a kind of the "energy capacity" measured by the work which the magnet can do before its "depletion". This capacity is highest for the relatively expensive magnets made of rare-earth metals, whereas much lower for the magnets made of the Alnico alloy.

The fact that magnets, in a great number of cases, do not lose their properties when doing work may be explained by only their "charging" from the ambient space. It is found that the permanent magnets, if shielded from the ambient space with a magnetic screen, will "deplete" much sooner in their operation under load. This will be confirmed hereafter based on the testing the Perendev Co's magnetic engines. In operation without load, as long-duration tests show, permanent magnet coercive force changes negligibly (from zero for the rare-earth magnets throughout 3% for the Alnico magnets for 10^4 test hours). This supports the idea that if a permanent magnet is kept far from power supply lines, other magnets, high temperatures and other factors affecting it adversely, this magnet will forever preserve its magnetic properties. Shocks and vibrations do not affect the modern magnetic materials unless and until they physically damage them.

The temperature of magnets dropping is a sure evidence of disturbing equilibrium between the electromagnetic field and the permanent magnets operating under load. This effect has been discovered in all without exception operable machines on permanent magnets. In the Floyd generator that temperature drop reached 20^0C. The energy exchange between permanent magnets and the ambience is not evidently restricted to the thermal radiation range. All bodies interpret the nonthermal radiation as work done on them. Such phenomena as photoeffect, photosynthesis, etc. evidence this. It is also known that the magnetic induction depends on the area electrons "cover" in their orbital movement and may not only decrease in the process of radiation or the work the permanent magnet does, but also recover in the process of electromagnetic wave absorption increasing the energy of the orbital electrons. Thus the "mechanism" of such energy exchange is in general known: this is the absorption of energy of various-frequency electromagnetic oscillations or some "radiation" energy differing from the directional flow of photons (radiant energy) by its isotropic character. This energy may be attributed to oscillations of the ether as an all-penetrating medium which stressed state causes the existence of the force fields. However, from the positions of thermokinetics as a non-hypothetic theory it does not matter. What really matters is only that in any case the admissible continuous power of magnetic engines is limited to the rate of their energy exchange with the power source. This means that, from the positions of thermokinetics, the permanent magnets should be treated in the same way as any other working media running through a cyclic process, and whatever “perpetual motions” are out of question. In this case the operation of the generators on permanent magnets may be shown as based on the same mechanisms as for other heat and non-heat engines. To this end let us use the basic equation of thermokinetics (2.4.5) which in our particular case looks like:

$$W_{\text{ц}} = \oint \mathbf{X}_{\text{м}} \cdot d\mathbf{Z}_{\text{м}} \, , \qquad (13.4.1)$$

where $\mathbf{X}_{\text{м}} = \mathbf{B}$, $\mathbf{Z}_{\text{м}}$ – magnetic induction and magnetization of the magnet in whole, respectively.

Let us consider, as before, the scalars $X_м$ and $Z_м$ and divide the circular process into two parts, 1–2 and 2–1, in which limits the $Z_м$ variation follows the same sign ($dZ_{\text{м}} > 0$ или $dZ_{\text{м}} < 0$). Then denoting $X_{\text{м}}$ in “there” and “back” directions with single and double prime, respectively, and considering $dZ_м'' = – dZ_м'$ gives instead of (13.4.1):

$$W_{\text{ц}} = \int_1^2 \left(B''_{\text{м}} - B'_{\text{м}}\right) \cdot dZ'_{\text{м}} \, . \qquad (13.4.2)$$

From this it follows that if the mean magnetic induction of a material is the same for both processes – its magnetization recovery (B'') and doing work (B') – there will not be any work done for the cycle. The said is illustrated in Fig. 13.8, where an arbitrary cycle of a magnetic engine is depicted, which resembles the minor hysteresis loop.

The work for this cycle is defined by the cycle area. Hence, it is necessary to somehow change the character of the “there” 1–2 and the “back” 2–1 processes for the cycle area to become other than zero. This may be provided through e.g. Serl effect (magnet self-rotation), or temporarily shielding the magnetic field in-between the rotor and stator at the stretch where the magnets are closest to each other, or varying the magnetic induction in the rotor or stator by temporary variation of their temperature (nearby the point of phase transition), or varying the path and field configuration when the rotor and stator magnets are moving to and off each other, or temporarily

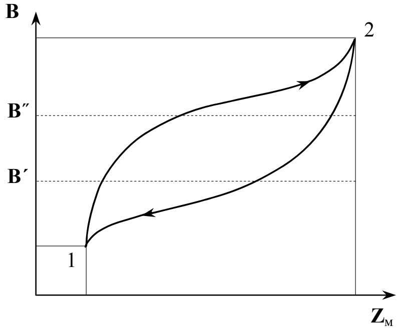

Fig. 13.8. Magnetic Engine Cycle

demagnetizing one of the magnets by electrical pulse at the moment of their opposition, etc. We will see hereafter these are the means the inventers of the permanent magnet-based devices of doubtless reality have recourse to.

The "Gramm's generator" (Z.T. Gramm, 1869) is among the first of such devices. It features a rotating annular rotor with the toroidal coil touching two conducting brushes diametrically opposite. The rotor rotates within the poles of a stationary permanent magnet. The "asymmetry" of the magnetization and demagnetization processes for the annular rotor was provided by shifting the moment of voltage supply to the toroidal coil.

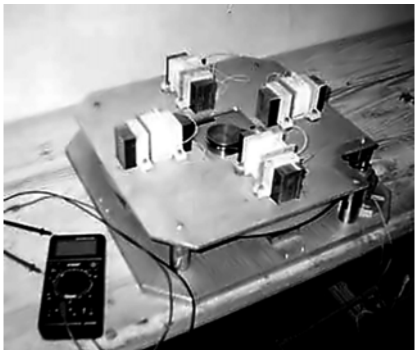

Fig. 13.9. Frolov's Generator

Later in 1996 Russian engineer A. Frolov upgraded the Gramm's generator. His design features a stationary ring with coils, while one more coil in the center is used as the alternative magnetic field source (Fig. 13.9). Two magnetic fluxes from the two load coils are mutually offset and, thus, there is no reaction in the primary circuit. This design concept has become popular (O. Berens, Sweden; D. Hofmann, USA; V. German, Germany; S. Hartman, USA; etc.). One of the designs based on this concept and termed by its authors as "Frolov's generator" is illustrated in Fig. 13.10.

The central permanent magnet is here set into rotation by a small-scale electric motor. To smooth the speed fluctuations, a massive flywheel applies (Fig. 13-9). In August 1999 V. German with his team in Germany succeeded to obtain more that 1,200W on load. In 2003 S Hartman (USA) designed a toroidal generator based on the standard 10kW-generator powered from a car storage battery. The generator input current was 0.8A at a voltage of 12.92V, the output current was 40A at a voltage of 6.5V. Thus the power obtained was 25 times over.

John. Ecklin offered in 1975 another way of the "asymmetry" creation (Patent USA No3879622 dated 22.04.75). His engine features magnetic shielding and opening in turns and includes two permanent horseshoe magnets, a motor rotating "windows" – magnetic shields, and a magnet keeper of magnetic material, which is in turns attracted to one of the magnets not shielded at the moment. The keeper swaying transforms into the rotary motion through a crank gear.

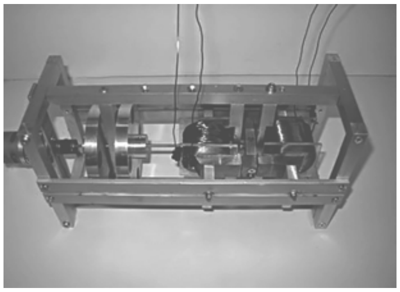

Fig. 13.10. German's Motor

The patent notes that with field strengths, magnet forms and materials, etc. properly selected the energy obtained through the translation motion can exceed the one necessary to open and shut the “windows”. Ecklin did not manage to create a “self-starting” machine, nevertheless, his concept served as a basic for a number of USA patents: Jaffe (No3567979, 1976); Monroe (No3670189, 1976); E. Gray (No3890548, 1976); V. Rivas (No4006401, 1977); H. Johnson (No4151431, 1979); F. Richardson (No4077001, 1987); D. Regan (No4883977, 1989); V. Hyde (No4897592, 1990); H. Aspden (No4975608, 1990), etc.

Some of the permanent magnets-based devices do not feature moving parts at all. The Vacuum Triode Amplifier (VTA) of S. Floyd’s design (USA) is one of them. Such a name is caused by the fact that the similar principle of governing powerful flux through weak signal is used in triodes. In the VTA design barium magnets were used prepared by repeated magnetic reversal at a frequency of 60Hz. That facilitated the transit of the field from one direction to another when applying a weak signal to the control winding from an external generator, thus, providing its “trigger” operation. One of the VTA designs under demonstration included two sets of the (4×6×1)-inch magnets positioned against two walls of the casing in such an arrangement that an attraction appeared between them. The axes of the output windings were parallel to the field lines, while the axes of the control windings were perpendicular to them. The output power of the Floyd’s device was partly looped in feedback to excite the process resulted in a significant power appeared in the output winding. Many investigators who successfully repeated the Floyd’s experiments (e.g. J. Naudin in France, whose design is shown in Fig. 13.11) noted that the best results of the magnetic substance “conditioning” were obtained when discharging alternate current arc of the same frequency as the control signal directly through the permanent magnet ceramics. Thus a bistable solid-state substance was created where acoustic resonance showed at the weak control magnetic field oscillation frequency.

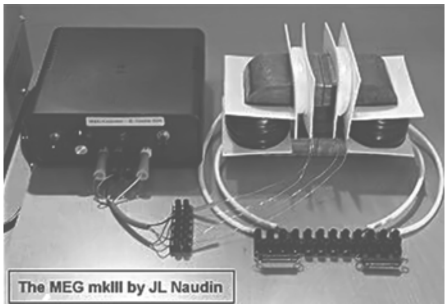

Fig. 13.11. Naudin’s Generator

Special attention is attracted to the current generators based on using the “self-sustaining rotation” effect of John Serl (Mortimer, Borkshire). In the fifties of the last century he discovered that adding a small alternate current (~100 ma) radio-frequency (~10 MHz) component in the manufacturing process of permanent ceramic magnets endued them with new and surprising properties. These consisted in the unusual interaction of the permanent magnet with the magnetic rollers located on its surface. That interaction showed in a spontaneous rolling of the rollers after applying a minor momentum to one of them.

In Russia the Serl effect was studied in the Institute of High Temperatures of Russian Academy of Science. V. Roschin and S. Godin, researches of this Institute, in 1992 built a generator similar to the Serl's one, which they termed the "magneto-dynamic converter". It constituted a stator with sector permanent magnets 1 and an annular rotor with rotating magnetic rollers 2 (Fig.13.12).

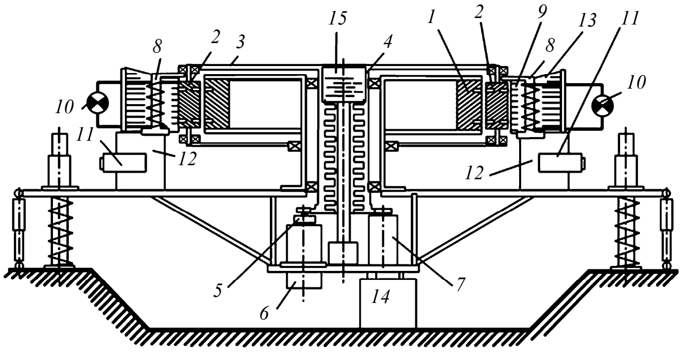

Fig. 13.12. Roschin–Godin's Converter

The rotor had a diameter of 1 m and a weight of 500 kg. The rotor segments were made on the basis of rare-earth magnets with a residual induction of 0.85 T. They magnetized by the bank of capacitors discharging through an inductor. Unlike the Serl's disc, the ac biasing was not used in the Roschin–Godin's device. The "engagement" of the rollers with the rotor annular magnet was provided to the gear principle through transversal magnetic inserts made of NdFeB with a residual induction of 1.2 T and arranged in the stator and the rollers. There was an air gap of 1 mm provided for in-between the stator surface and the rollers. The elements of the magnetic system were assembled as a unit construction on a platform made of non-magnetic alloys. The platform was equipped with springs, dampers and was free to move vertically along three guides, which was measured by an inductance transmitter 14. The stator 1 was fixed, while the rollers 2 secured on a mutual movable separator 3 with the help of air dynamic bearings. The separator was rigidly coupled to the shaft 4 and, through friction overrunning clutches 5, to the starting motor 6 and electro-dynamic generator 7. There were electromagnetic transducers 8 with open magnetic conductors 9 positioned along the rotor. The load 10 was arranged as electric incandescent lamps. The machine was put into operation by speeding the rotor up from an electric motor. At ~550 rpm the speed of rotor rotation became spontaneously increasing despite the motor stopped with the electro-dynamic generator coupled to the shaft. To keep the speed, a load in the form of tubular electric heating elements was stepwise connected to the generator. The power output of the machine was 7 kW.

There were a number of unusual effects observed in the machine besides the “surplus power” generation, viz. platform weight reduction (to 35% of the initial weight); corona discharge in the form of a blue-pink glowing; vertical concentric zones of increased magnetic intensity (to order of 0.05 T) and abnormal temperature fall (by 6^0C–8^0C) in close proximity to the converter. The impossibility of the existing theory to explain all these effect in whole evidences its deep inferiority.

An interesting version of a switching-reluctance device generally recognized as one of the most successful “free-energy” engines was offered by Robert Adams (New Zealand) in 1977. In the Adams’ motor-generator (Fig. 13.13) a rotor having permanent magnets with like poles oriented radially outside rotates generating inductive currents in the stator coils positioned around the rotor in the plane of rotation. From the traditional electrical engineering standpoint a motor-generator without the closed core (coil cores have the bar configuration) is inefficient. However, this is the open core that makes it possible to generate power without rotor braking. There is no the electromagnetic induction phenomenon here in the true sense of the word, but only the magnetic induction, i.e. the magnetization and demagnetization of the stator core in the rotor permanent magnet field. It may be seen a full analogy with the electric induction, i.e. the “electrization by induction” as they would say before. The “electrization by induction” differs from the electromagnetic induction since the secondary magnetic field generated in the generator winding does not decelerate the rotor and does not interact with the primary magnetic field. Robert Adams is working together with H Aspden on acquisition of patent for his system. It is significant that operability of this machine can be completely explained as based on the Faraday’s law.

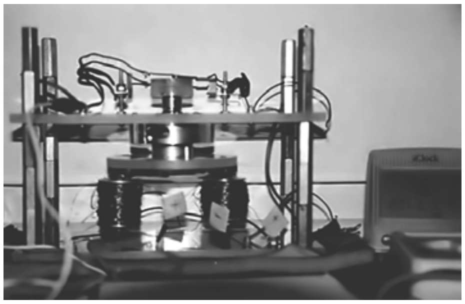

Fig. 13.13. Adams’ Motor

The K. Minato’s wheel (Patent USA No5594289, 1997) is another rotating magnets-based engine even more attractive for

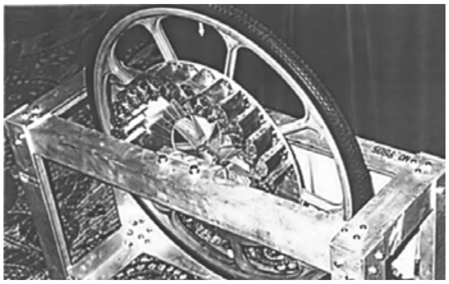

Fig. 13.14. Minato’s Wheel

reproduction. It consists of a rotor (a bicycle wheel rotating on a horizontal axis) having a multiplicity of permanent magnets attached and with their like poles oriented in the rotor rotation direction, as well as stabilizers intended to balance the rotor (Fig. 13.14). Each of the permanent magnets attached to the rotor is positioned at an angle to the wheel radius. An electromagnet with electric current periodically induced depending on the rotor rotation is arranged nearby the external periphery of the rotor closely to it. Eric Vogels (Sweden, 1997) repeated and improved the Minato's results having split the track of the magnets into a multiplicity of minor tracks.

Many patents on magnetic engines have been granted in Russia (V. Alekseenko, No5037775, 1996; V. Rykov, No2000101256, 2001; A. Rjumin, No2001123502, 2003; V. Levkin, No5032711, 1995; M. Ostrikov et al, No95103846, 1996; A. Starostin et al, No95112010, 1997; A. Kalinin, No94019782, 1996; P. Imrish, No94026259, 1996; V. Dudyshev, No2128872, 1998; Y. Pilipkov, No2000119415, 2002, etc).

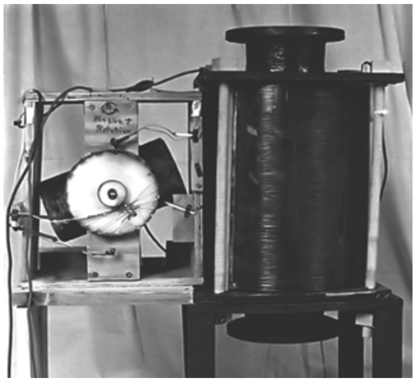

Fig. 13.15. Newman's Engine

American television network recently released the information about a revolutionary technique developed by J. Newman. His electromagnetic motor (Fig. 13.15) is capable to power a production area, residential building or farm. It is based on the concept that the motion of electrons in coil wires resembles the motion of micro-gyroscopes as electrons rotate. For high-inductance coils this motion engenders special effects showing in the "surplus power" generation. It is significant that more that 30 physicists, nuclear engineers, electrical engineers and electricity experts signed the letter that confirmed the revolutionary character of that invention.

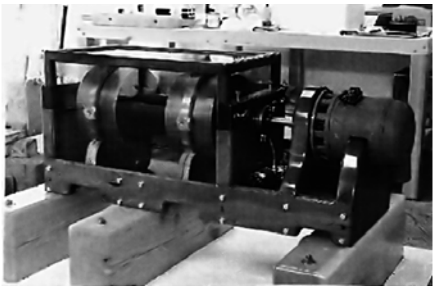

Fig. 13.15. De Palma's Generator

The homopolar induction effect known yet from Faraday's time is also capable to create electromotive force at the rotation of a metallic rotor. De Palma's homopolar generator (1991) is one of the practical designs the alternators of this class feature. The testing results on this generator (Fig. 13.16) show that its rotor deceleration due to the back EMF appears to a less degree than in the traditional generators. Therefore, system power output surpasses that required for the rotor rotation.

It is worth noticing that the creation of the alternators has already gone into a practical development stage. Swiss company SEG has quite recently announced its intention to bring to the market a generator operating on the Serl effect. It is planned to launch in the first place a compact 15-kW generator with approximate size parameters of 46×61×12 cm, which can be tuned to generate direct or alternate current of various voltage within a range of 12V to 240V. Each of such generators is capable to produce 60MW/h of energy before the reversal of the polarity would become necessary. The generator model D15AP offered is illustrated in Fig. 13.16. It consists of three four-layer concentric rings, each of the rings being made of composite. The rings are concentric to each other and attached to a base. Rollers freely rotate around each of the rings: 10 pieces around the first ring, 25 – around the second ring and 35 – around the third one. There are coils arranged outside the rollers at the external ring periphery. The coils are connected in different manner, which enables generating either direct or alternate current of various voltage. The output coils have to be calculated to provide an output voltage of 240V at a power output of 15kW. The generator is a set of frictionless bearings in a way and, at the same time, a system of three rotary transformers in one casing with a current of an extremely high voltage at the output.

Fig. 13.16. Serl's Generator

The LUTEC generator of Australians Brits and Christie (International Patent No00/28656, 2000) has been one of the recent additions to devices of this class. The simplicity of this engine is provided by arranging switchable coils on the stator, while a permanent magnet – on the rotor. The direct current input to the stator coils causes the magnetic repulsion force and is the only current to create the "aggregate motion" (Fig. 13.17).

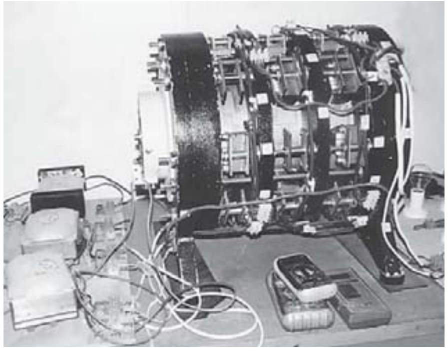
Fig. 13.17. LUTEC Generator

A number of private enterprises are currently taking orders for commercial motor-generators on permanent magnets. In particular, the GMC Holding Corporation (Orlando, Florida, USA) claims that as a result of the 12-year study it has created a device on permanent magnets capable to solve the world economic problems in power engineering. Another company, Perendev (abbreviation of "perpetuum energy device") claims that a 30kW-magnetic motor of its production is ready to find market acceptance (Fig. 13-18).

Cost estimate of the first devices is about 8,500 €. Truth to tell, Keith Anderson, whose company was invited to test the Perendev motor and built two operating analogs, claims all of them depleted their load magnets. Hence, further investigations are necessary to clarify the balance conditions for the internal energy the magnets release and their replenishment from the ambience. The key problem of the designs on permanent magnets is to calculate the magnetic flux distribution in the magnetic circuit that may include permanent magnets, air gaps, high magnetic permeability elements and electrical currents. Accurate solutions on magnetic fields demand a complicated analysis of many factors, though approximate solutions are also acceptable based on certain simplifying assumptions. To obtain an optimal design with permanent magnets, an experience and trade-offs are often needed. Meantime, the Perendev company takes orders from those who have the adventurous spirit alive and appreciate risks and restraints of this early stage.

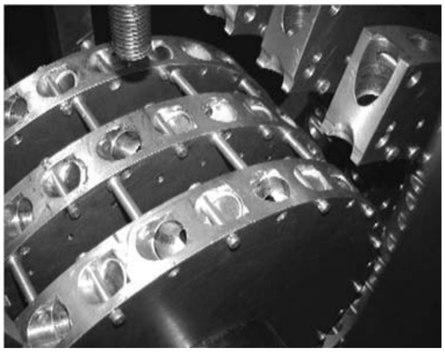
Fig. 13.18. Perendev Magnetic Motor

One more magnetic engine modification called as Cycclone[1)] has been recently created on funds of an American company in Australia (Fig. 22-19). A demonstrational prototype of this engine intended for a car application was shown on TV.

[1)] The name reflects the engine combines cyclic motion with magnetic field "cloning".

It is quite evident that when estimating the availability of such devices it is impermissible to consider the magnetic energy as "gratis" – its prime cost needs the same expense accounting as for any other power units on renewable power sources. These expenses depend on the magnet classes. The samarium-cobalt (SmCo) and neodymium (NdFeB) magnets sintered from rare-earth elements are the newest addition to the earlier known ferrite (ceramic) and aluminum-nickel-cobalt (Alnico type) magnetic materials. They feature the magnetic energy level achieved as 45–50 MGOe (mega gauss oersted). The recent developments in the magnet fabrication technique contributed to this achievement. These developments have opened new thrilling vistas toward technology upgrade of the permanent magnet engines. Besides their production costs it is reasonable to estimate also the efficient design effort and theoretical in-depth studies since the impossibility to explain the multiple effects revealing themselves in application to the alternators in operation evidences that theory is far behind experiments.

Fig. 13.19. Cycclone Engine

Thus we can expect the market will see small-scale power units capable to efficiently power offices, residential buildings and farms located far away from power transmission lines.

In conclusion it is desirable to underline that despite the fact the operation of alternators is obscure in many respects there are enough grounds at present to search for the most successful technical solutions on creation of new-generation converters using the practically inexhaustible energy of the ambient space.

13.5. Converters of Radiation Field energy

A dozen phenomena are known to date where after the "activation" of some working medium the heat generation during its relaxation exceeds the energy input. Such a "production" of heat energy may be observed in the oxygen–hydrogen electrolytic tanks on usual and heavy water (V. Filimonenko, 1957; S. Johns, 1989), in the electrical arresters (A. Chernetsky, 1971); vortex heat generators (Y. Potapov, 1992); at plasma and plasmachemical dialysis (A. Frolov, 1998; F. Kanarev, 2001); at "sonoluminescence" (R. Taleyar Khan, 2002), etc. Although such phenomena were discovered a long time ago (F. Latchinov, 1888), these became known to most people after Stanly Pons and Martin Fleishman, researchers of the Utah University, had reported the results of their experiment they construed as the "cold thermonuclear fusion". Pons and Fleishman claimed they had observed a heating of the electrochemical element that used heavy water as an electrolyte. In that case the heat released much exceeded the electric power consumed. Fleishman assumed that the energy was generated inside the palladium cathodes in the course of the nuclear reaction where two deuterons combined into ^{4}He in some manner yet unknown. However, no products of that reaction were discovered which would correspond to the heat generation as claimed. The scientific community did not recognize that claim for a scientifically substantiated explanation for several reasons. Firstly, the Coulomb barrier impedes the combination of deuterons at room temperature. The mechanism when deuterons could approach each other so that the synthesis would occur was unknown. Secondly, if they could approach each other for a reaction to occur, usual synthesis products should have been observed as they appear very soon. Thirdly, a reaction when two deuterons combine and form ^{4}He usually runs with releasing gamma rays of order of 24 MeV. However, such a flow of gamma-ray emission was not observed during the experiment. Finally, the reaction in whole ran a million times faster than at usual conditions. Therefore, after many of the laboratories that attempted to reproduce that experiment had failed the scientific community came to a conclusion that the data of those experiments was incorrect. Meantime, yet in 1989 S. Johns made another statement that during electrochemical reactions in heavy water he had observed the deuteron synthesis reaction. The scientific community's response to that statement was skeptical as well since the signal/noise ratio was minor, while the theoretical considerations did not allow treating as significant the effect Johns overstressed.

Therefore, it was an unexpected sensation when in 2002 the extremely prestigious scientific magazine "Science" published an article about a desktop thermonuclear unit R. Taleyar-Khan's team (USA) had created. There a small cylinder containing acetone with the hydrogen nuclei replaced by the deuterium ones was irradiated with a powerful flow of acoustic waves simultaneously with a neutron flux. The operation of the unit was claimed to have been based on the sonocavitation effect when the acoustic waves shook the water thoroughly having a multiplicity of bubbles produced there with a diameter of to 1 mm (much greater than usually), which then "collapsed". Something like this has been known since yet the thirties when it was discovered that some substances started to glow when ultrasound was passed through them (a phenomenon known as the "sonoluminescence"). Physicists affirmed that in that case acetone was heated to such temperatures that the deuterium nuclei started to merge. As in the case with the "cold thermonuclear fusion", the investigators immediately encountered troubles. The magazine "Science" that can not hazard its reputation when publishing the like sensations without credibility check gave the floor to also other investigators who attempted to reproduce the experiment. They also discovered the neutrons. However, when they started to measure the neutron flux with a detector more advanced than in the initial test, the particles immediately disappeared. Besides, nothing proved those neutrons had something to do with the thermonuclear reaction. As a result, a good part of scientists came to a conclusion the process of such a kind just did not exist in nature.

Nevertheless, a number of investigators continue to insist on the fact that the water itself is the source of energy in such phenomena. They often refer herein to an installation known as the "Patterson cell" (USA). This installation is an electrolytic element filled with fine plastic beads covered with superfine layers of nickel. The latter, like palladium, is capable to collect and hold the heavy isotopes of hydrogen. When current is passing through the layers, electric charges appear on them. Such a device, according its producer – Patterson Power Cell (USA), steadily outputs 5W of heat power per each 1.5W input. In Patterson's opinion the "surplus" heat in his device appears due to the cold nuclear fusion. The Patterson's electrolytic thermal cells are currently produced by the ENECO Corporation that has collected above thirty patents with key technological solutions into a unitary patent package. The Nova Resources Group Inc. (Canada) has also launched the cells into production.

However, the physical proofs the advocates of the "cold nuclear synthesis" theory and of water as the "energy of future" source adduce are so dubious that many investigators are inclined to call it after R. Park the "voodoo science". To make sure that some effects of the "cold nuclear synthesis" are not the reason, but rather consequence of an external impact on a system, it is enough to consider the operation of the machines wherein the "surplus heat generation" is observed at the conditions when the nuclear synthesis is excluded.

The quite sensational results Stanly Myer obtained confirming the resonance effect of electrostatic field on water molecules are among most known. In the late eighties he developed and fabricated a "low-current" water fuel electric cell (Fig. 13.20) that makes it possible to separate the usual tap water into hydrogen and oxygen with much less energy consumption than at the usual electrolysis. As S. Myer's investigations showed, when water is exposed to a frequency coinciding with its natural molecular frequency, the chemical affinity of the hydrogen and oxygen obtained (generated as heat in the process of their subsequent synthesis) appears to exceed the energy consumed from the current source.

The design of the Myer's cell is simple. Its electrodes are made of stainless steel plates either parallel or concentric. The gas output is usually proportional to the distance between them – a good result is assured with a patented distance of 1.5 mm. Considerable distinctions from the usual electrolytic cells lie in the power supply to the cell. Myer uses an external inductance that forms an oscillation circuit with a cell capacitor to create a parallel single-tuned network. It is actuated by a powerful pulse oscillator that along with the cell capacitor and a rectifier diode constitutes a pumping circuit. The high frequency of the pulses generates an in-step rising potential until the point reached where the water molecule disintegrates and a short current pulse appears. The meter-current supply circuit reveals this step and locks the impulse source for several cycles allowing the water recovery. Whereas the usual water electrolysis requires a current measured in amperes, the Myer's cell provides the same effect at millamperes. Furthermore, usual tap water requires an electrolyte (e.g. sulfuric acid) to be added to increase conductivity, whereas the Myer's cell operates with pure water providing a tremendous throughput. According to eye-witnesses the most striking aspect of the Myer's cell was that it remained cold even after several hours of the gas production. The recorded gas output was enough to show the oxyhydrogen flame that instantly melted the steel. To say nothing of the abundant release of oxygen and hydrogen and minimal heating of the cell, it was surprising that the water even inside the cell disappeared quickly having transformed into its components in the form of a mist spray as a great number of tiny bubbles that covered the cell surface. Myer claimed his oxyhydrogen mix converter was working for last four years based on a chain of six cylindrical cells. The Myer's invention is covered by a series of USA patents (Patents 4.936.961, 4.826.581, 4.798.661) filed before 1991 under heading "101" (where granting a patent for invention is subject to its successful demonstration). The inventor explains the cell operation by the polarization of water molecules under the electrical field gradient and the resonance within the molecule, which enhances the effect. This standpoint is close to thermokinetics which considers the low-current electrolysis as a remarkable example of the work done by high-frequency electromagnetic oscillations applying the resonance effect to the electrons relatively weak-retained.

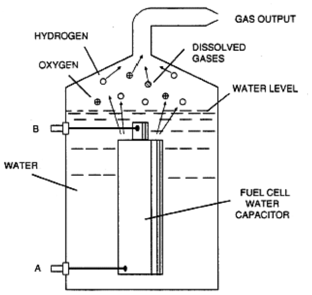

Fig. 13.20. Myer's Cell

Some investigators explain the surplus heat appearing by the water molecular structure reconfiguration. Actually, tens of the water molecular structure modifications are known which evidently differ in also their internal energy. In such a case the water transit from one configuration into another with a lower energy level must involve a heat release. In particular, as Dr. R. Mills (USA) sees it, the hydrogen atoms in the water molecule may be at different energy sublevels including also those corresponding to fractional quantum numbers. He called the water molecules with hydrogen atoms being at a lower (than usual) energy level as “hydrino” (see also S. Nesterov, 1995). However, this standpoint contradicts quantum physics and meets, therefore, many opponents.

Meantime, there may exist another and quite adequate to the existing paradigm explanation of the surplus heat release phenomenon in the above processes. For this it is necessary to recognize the fact that the “heat generators” above described operate as heat pumps. They feature the reverse cycle “water electrolysis – hydrogen and oxygen synthesis” where the dissipated radiant environmental energy is a heat well analog, while the work spent for electrolysis – an analog of compression work in heat engines.

Released heat Q to power supply energy W ratio called as heat transformation coefficient η_T in thermodynamics is known to be the efficiency criterion for inverse cycles:

$$\eta_T = Q/W > 1, \tag{13.5.3}$$

This criterion always exceeds unity if only W is construed as the work a source of current supply spends. However, this not at all means the “over-unity” efficiency $\eta_t = W/Q$ obtained since the efficiency is construed as a reciprocal, viz. work W obtained in engine related to heat Q supplied from ”hot’ well.

The experiments conducted by Wm. Lyne (1996) are further evidence that the field (distinguished from substance) forms of energy of the ambient space are a source of surplus heat energy at the spontaneous synthesis of hydrogen and oxygen molecules in the Myer’s installation. In 1981 Lyne built and tested a heating system on atomic hydrogen. The hydrogen in his installation, like at the usual hydrogen welding, passed through electric arc which decomposed it into “atomic” hydrogen. Then the atomic hydrogen recombined under heat release. Thus the hydrogen played a part of a “mediator” that ran through a cyclic process, while the electric power consumption to maintain the arc was considered by Lyne as an “activation” energy. The energy “lacking” for the hydrogen dissociation was taken, in Lyne’s opinion, from the “ether”.

Similar results are obtained in tests with heat generators on atomic hydrogen, which have been conducted in Russia since 2003 by A. Frolov, founder of the Faraday Lab. Ltd (JSC LNTF). His design is based on a powerful electron-vacuum diode with the tungsten directly heated cathode (Fig. 13.21).

The generator includes a cylinder with inlet and outlet channels where the water stream flows around a closed internal chamber filled with hydrogen at a pressure of 0.2 at. The diode tungsten filament with a diameter of 0.25 mm in the center of the device serves as a cathode whereon the hydrogen changes from molecular state into atomic one. Then during the H–to–H_2

transit a “surplus” heat is released, which is removed with the cooling water. Hydrogen is not consumed here. To create the “low-current” splitting of H_2 into H, a potential difference with pulses within 200 V to 300 V is applied between positive anode and negative cathode. The pulses are generated by direct current with a frequency of to 10 MHz. When using the cathode pulse heating of 12 V with a frequency of 51 Hz and a pulse/break ratio of 5%, a multiple excess of the heat produced over the electrical power consumed is obtained. It is significant that the anode voltage pulses generated by alternate current do not cause this effect. These experiments obviously enough confirm the above “thermokinetic” interpretation of the “surplus” heat production origin. The absence of the hydrogen consumption evidences that hydrogen is here just a “mediator” (working medium), but not the energy source, while the absence of the “surplus heat generation” effect with ac supply to anode confirms the fact that this effect is obtained not by the “excitation” of orbital electrons at their mean energy level invariable, but rather by the unilateral action of the voltage pulses in the direction of removing the orbital electrons from the hydrogen nucleus (in resonance with pulses of the electromagnetic field surrounding the device). The selection of the anode voltage pulse frequency is necessary in this case in order to obtain resonance between the external field action and the “activation” pulses.

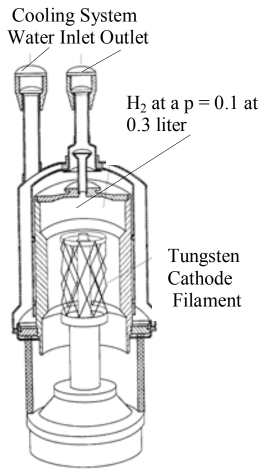

Fig. 13.21. Frolov’s Generator

French investigator J. L. Naudin has recently improved the operation of this generator replacing the power unit by a large-capacity battery with a 10 MHz-pulse generator. On this basis Naudin managed to better form the anode voltage pulse, which configuration appeared have been very important, and thus to build up the “heat output”. His “atomic hydrogen generator” was in operation for an hour with an efficiency exceeding 2,000%, i.e. with 20-fold exceed of the heat generation over the electrical power consumed. He used two types of absolutely different measuring instrumentation which confirmed the reliability of input power measurement for the installation.

Y. Potapov’s “heat generator” (Patent of RF No2045715, 1993) is one of the widely known devices intended for practical using “surplus” heat generation. It constitutes a vertical cylindrical tube with a water flow tangential input in its upper part (Fig. 13.23). The velocity of the water is such that there are cavitation phenomena causing quick water heating and observed in the tube along with the intensive flow turbulence. If this water is removed from the maximal temperature zone and directed to usual heating devices with return to the lower part of the vortex tube (wherefrom it is taken by a usual centrifugal pump and pumped again to the upper part of the tube), the amount of the heat removed for heating appears to exceed the amount as to the balance of the dissipative (hydrodynamic) losses for friction and cavitation. From the author's initial statements his heat generator produced up to 3 to 4 kW of heat per 1 kW of the electrical power consumed. However, at comparative testing in NPO «Energia» in 1996 the heat generation in the Potapov's device appeared to have been only 23% higher that in the 3-phase ac electrode boiler and 42% higher than in the electrical boilers with standard heating elements (tubular electric heating elements). In Potapov's opinion the surplus heat generation in his installation is explained basically by the integration of water molecules in "associates" under the cavitation effect and, to a lesser degree, by the cold nuclear fusion reactions (Y. Potapov et al, 2002). This standpoint is supposedly supported by the discovered in the HPO «Energia» 1.5-increase in the hard gamma radiation (not mitigated with steel shield) and the generation of carbon radioactive isotopes if the installation filled in with an anti-freezing agent.

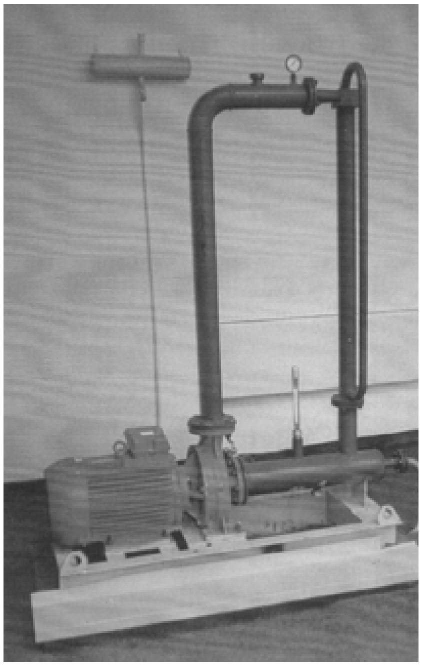

Fig. 13.23. Y. Potapov's Heat Generator

At the same time the author has repeatedly stressed that the water in the installation may not be interchanged for several years. This means that the water and the anti-freezing agent were actually just a working medium participating in the closed process, whereas a primary energy source should be searched for beyond it. This is the opinion F. Kanarev (2004). He thinks physical vacuum to be the "surplus" heat generation source.

The surplus heat generation phenomenon theoretically allows creating autonomous (self-sustained) power supply sources. To create them, it is necessary to combine electrolysis cell with fuel cell or heat engine converting heat *Q* obtained at burning of oxyhydrogen mixture into electric power *W*. According to thermodynamics the efficiency of such a machine will be dependent on the temperature *T* of the heat *Q* yielding from synthesis or recombination. If the temperature of the heat obtained as a result of synthesis or recombination exceeds that of the ambient space $T_o \approx 300$ K by just 30K, ideally the Carnot engine built on this heat source will have the thermal efficiency only 9%. This means that, to cover the energy expended on electrolysis, a more that 11-fold "surplus heat" output is needed.

Nevertheless, the thermokinetic analysis undertaken herein is meant to mitigate the suspicion of formal science toward the phenomena above described and to switch the problem of creating electrical energy alternative sources to practical course. Several firms are already selling cavitation heating equipment. Formal science is looking askance at this trade activity, the more so because the surplus heat generation in this equipment is not supported with independent expert appraisal data. However, profit of trade appears to be dominating. As reported at the Genesis World energy consortium's site, they have already developed a self-contained and self-sustained energy generator "Edison Device". In its size it is approximates to the external air conditioning system, which makes it possible to quickly and easily install it at home or in office to obtain a practically unlimited energy from any available water source. The commercial model of the device is capable to generate 100 kW of energy per diem. The "mechanical part" comprises minor pumps and micro-valves providing a circulation, which makes the device noiseless and not demanding a special maintenance for the designed 20-year service life. The feasibility of such environmental energy converters are also confirmed by the valid tests on the Mayer's converters in motor car application. Water consumption per a haul of 100 km was there about 3 liters (Pat. USA No 149.407). Thus the point is just to find the most promising engineering solutions in this field.

Conclusions

Applying thermokinetic to systems doing useful work has made it possible to set and solve a number of new interesting problems. Laying foundations of similarity theory for linear power converting systems should first of all be noted among them. This theory has first confirmed in most general the unity of general regularities of energy conversion in heat and non-heat, cyclic and non-cyclic, direct and inverse machines. It has thereby uprooted the inconsistency of attempts to restrict the application of classic thermodynamic laws to only heat engines. Practical importance of this theory is that it allows transferring the investigation results from one (well studied) power and process installations to another (little studied). The examples given in this chapter confirm this.

Laying foundations of productivity theory for technical systems has become not less important achievement of thermokinetic. Enabling the synthesis of thermo-kinetics and thermo-economics this theory supplements the classic analysis of thermodynamic efficiency for power units by correlating their power and economic efficiency. Thereby it approximates the thermodynamic estimates of limiting potentials for irreversible processes to reality. At the same time this theory allows finding the economically most advantageous operational modes for various power, process and transport units, which is of great practical importance. The theory application examples given in this chapter demonstrate that the conclusions from thermokinetic are of the same strictness and generality degree as those from thermodynamics with regard to reversible processes.

However, most "exotic" are perhaps the deductions of thermokinetic about the possibility of using field forms of energy. These results allow explaining the functionality of a number of devices presently referred to "perpetuum mobile". The hermokinetic analysis given in this chapter and pertaining to devices consuming the energy of gravitational, electrostatic and electromagnetic fields demonstrates that the operation of these devices does not exceed the bounds of thermokinetic and does not conflict with its laws. Lifting theoretical bans on creation of such devices opens new vistas to using renewable energy sources alternative to the known ones and actually inexhaustible.

Part 5

EXTENSION OF ENERGY TRANSFER THEORY APPLICABILITY

Various thermo-mechanical, thermo-diffusive, thermo-electrical, thermo-magnetic, etc, effects widely used in modern heat engineering devices and arising with dissimilar non-static processes simultaneously running in the same domains of space have given rise to a keen interest of science and engineering in boundary fields of knowledge. This causes the necessity to synthesize the heat engineering fundamentals with other scientific disciplines. One of such attempts was made in thermodynamics of irreversible processes. However, the theory of irreversible processes (TIP) was constructed by extrapolating classic thermodynamics beyond the strict framework of applicability of its system equilibrium and process reversibility concepts. This has led the TIP to its losing the rigor and completeness intrinsic for the classic thermodynamic method. In this context it becomes a question of significant importance to provide a consistent thermodynamic substantiation of the TIP fundamentals from the more general positions of thermokinetics.

Chapter 14

THEORY OF NONLINEAR TRANSFER PROCESSES

This chapter is dedicated to a new method proposed to find and describe these effects. The method consists in finding for each of the independent transfer processes a resultant force which disappearance ceases the process. The method allows to dramatically facilitate the thermodynamic description of irreversible processes and to cut the number of the kinetic coefficients required for such a description. It casts light upon the origin of the so-called stationary superposition effects for different-kind processes, which will be obtained here from the conditions of partial (incomplete) equilibrium as a result of mutual compensation of the components the resultant force consists of.

The effectiveness of the method proposed and the validity of the conclusions received within the frames of thermodynamics will be confirmed here by ample experimental data.

14.1. Proof of Existing Motive Forces' Resultant in Independent Transfer Processes

When having extended the L. Onsager's formal theory of velocity to the vector transfer processes, H. Cazimir (1945) and I. Prigogine (1947) kept to the same concept according to which any of the independent flows $\mathbf{J}_i$ was linear with all the thermodynamic forces $\mathbf{X}_j$ acting in the system, i.e. they used the same Onsager's law (4.1.6) but with the scalar flows J_i and forces X_j substituted there for the vector values $\mathbf{J}_i$ and $\mathbf{X}_j$. Thus obtained kinetic equations (4.4.1) added to known Fourier's, Ohm's, Fick's, Darcy's, Newton's, etc. laws the "non-diagonal" terms $L_{ij}\mathbf{X}_j$ which characterized the contribution of the "alien" force $\mathbf{X}_j$ to the i^{th} flow $\mathbf{J}_i$ ($j \neq i$). E.g., to describe the thermo-diffusion phenomenon (the k^{th} substance flow arising under a temperature gradient) the right side of the Fick's law of diffusion is added with a linear term proportional to the temperature gradient. This is equivalent to representation of the flow $\mathbf{J}_i$ as a sum of several summands $\mathbf{J}_{ij} = L_{ij}\mathbf{X}_j$:

$$\mathbf{J}_i = \Sigma_j\, \mathbf{J}_{ij} = \Sigma_j\, L_{ij}\,\mathbf{X}_j\,. \tag{14.1.1}$$

Such a description corresponds to a notion that the non-matching flows running simultaneously in the same space areas are as if "superimposed" each one onto other (S.R. De Groot, P. Mazur, 1964) mutually "entraining" and intensifying each other (A. Veinik, 1973; N. Bulatov, A. Lundin, 1984). More than half a century this notion has been indisputable and reproducible in all study guides on thermodynamics of irreversible processes but with a proviso that, according to Curie symmetry law, only processes of the same (or even) tensor order and kind can interact (be superimposed) (S.R. De Groot, P. Mazur, 1964). This law first substantiated by P. Curier (1947) stated that due to the possible spatial symmetry in anisotropic systems the number of coefficients in linear equations would decrease in such a way that not all Cartesian flow components would depend on the force components. However, it appeared important for isotropic systems, too. As De Groot and Mazur showed (1964), in anisotropic systems the Cartesian components of thermodynamic forces of different tensor order and kind would be transformed at rotation and inversion in such a way that only the links between the same tensor-order flows and forces would remain invariable. Thus for isotropic systems the Curie law may read as follows, "*In isotropic systems the phenomena described by thermodynamic forces and flows of different tensor order and kind do not influence each other* (I. Gyarmati, 1974). In other words, any vector flow $\mathbf{J}_i$ may depend on only forces of the vector character.

The investigators were not at all confused with the fact that the Onsager's postulate disagreed with the centuries-old foundations of mechanics according to which each independent process (movement, acceleration, setting of mechanical equilibrium, etc.) could be associated with the only (resultant) force which disappearance would cease the process. The anisotropic heat conduction and electric conduction equations, which, as Onsager admitted, had prefigured his "phenomenological" laws, also evidenced the motive force uniqueness. The components of the only motive force – temperature gradient and electric intensity, respectively – were in those equations under the sum sign, too. Ultimately, it was not at all a secret that the said "superposition effects" reached their extremum at the so-called stationary conditions when some (the so-called "non-fixed") flows simply disappeared and therefore could not in principle be superimposed onto the remainder flows. E.g., in electrolytic solutions, where the phenomena of electric conduction and diffusion take place, the voltage (Quincke effect) is maximal with the current disappeared. (Haase, 1967). The same situation is about Soret effect – generation of the k^{th} substance concentration gradient within the initially homogeneous system with a temperature gradient generated, the said concentration gradient reaching peak value with the diffusive flows disappeared. Hence the reason of such superposition effects arisen should have been searched for anywhere but not in the interaction (superposition) of the irreversible phenomena themselves. In fact, the generation of gradients or differentials of whatever potentials meant the system withdrew from that kind of equilibrium, i.e. anti-dissipative processes appeared in the system. Meantime any relaxation phenomena are always directed toward setting equilibrium. In other words, the components $\mathbf{J}_{ij}$ of the generalized rate $\mathbf{J}_i$ of any relaxation process in (5.1.3) have always the same sign. Therefore some of these flows $\mathbf{J}_i$ becoming zero in stationary state could be caused by only mutual compensation of the components $\mathbf{J}_{ij}$ of this flow. However, all terms in equations (14.1.1) have intrinsically the same sign as they describe the relaxation processes. Hence the appearance of the "superposition effects" could have been explained by only the generation of anti-dissipative processes in the system. However, the investigation of such processes was evidently beyond the Onsager's theory. Therefore such an assumption could not arise in its depths.

To reveal the fallacy of the Onsager's postulate, let us note that the coefficients L_{ii} and L_{ji} in the components $\mathbf{J}_{ii} = L_{ii}\,\mathbf{X}_i$ and $\mathbf{J}_{ji} = L_{ji}\,\mathbf{X}_i$ of flows (14.1.1) are expressed in terms of the matching components $\mathbf{J}_{ii}$ and $\mathbf{J}_{ji}$ of the flow $\mathbf{J}_i$:

$$L_{ii} = d\mathbf{J}_{ii}/d\mathbf{X}_i\,;\; L_{ji} = d\mathbf{J}_{ji}/d\mathbf{X}_i\,. \qquad (14.1.2)$$

According to (14.1.2) there is a simple relation between the diagonal L_{ii} and non-diagonal ("cross") coefficients L_{ij} of the transfer equations in matrix form:

$$L_{ji} = L_{ii}\,(d\mathbf{J}_{ji}/d\mathbf{J}_{ii})\,. \qquad (14.1.3)$$

However, at $\mathbf{X}_j$ = const $d\mathbf{J}_{ji} = d\mathbf{J}_j$ and $d\mathbf{J}_{ii} = d\mathbf{J}_i$, therefore (14.1.3) may be changed to:

$$L_{ji} = L_{ii}\,(\partial\mathbf{J}_j/\partial\mathbf{J}_i)_{Xj}\,. \qquad (14.1.4)$$

From this it follows that providing the flows $\mathbf{J}_i$ and $\mathbf{J}_j$ are not interconnected, the coefficients L_{ji}, at $\mathbf{X}_j$ = const, become zero along with the derivative $(\partial\mathbf{J}_j/\partial\mathbf{J}_i)_{Xj}$. This means that for the independent flows $\mathbf{J}_i$ and $\mathbf{J}_j$ the reciprocity relationships are satisfied trivially ($L_{ij} = L_{ji} = 0$) just as expected. In other words, in the absence of the motive force $\mathbf{X}_i$ as matching the flow $\mathbf{J}_i$ no other force whatever can induce this flow providing it is truly independent. Since the independence of the flows $\mathbf{J}_i$ and $\mathbf{J}_j$ is laid into the foundation of the Onsager's theory by the flow $\mathbf{J}_\mathrm{i}$ definition as itself, kinetic equations (4.1.6) are really valid for interconnected flows.

So in the absence of additional constraints imposed the Onsager's postulates should be superseded by a statement reading that *the generalized rate of whatever irreversible process (flow* $\mathbf{J}_i$*) depends on only the components of the sole(resultant) motive force* $\mathbf{F}_i$. This statement corresponds to the kinetic transfer equations of the (2.6.11) kind:

$$\mathbf{J}_i = K_i(\mathbf{F}_i - \mathbf{F}_{io}) = L_i(\mathbf{X}_i - \mathbf{X}_{io}), (i = 1, 2, ..., n_i) \qquad (14.1.5)$$

where the coefficients $\overline{K}_{ij} = K_i(\Psi_j, \mathbf{F}_i)$, unlike (4.4.1), are arbitrary functions of thermostatic parameters (temperature, pressure, concentrations of the k^{th} substances, etc.), as well as of any forces $\mathbf{F}_{\text{i}}$. The principle difference of equations (14.1.5), besides their non-linearity and the "threshold" values of the forces $\mathbf{F}_{i\text{o}}$ which can be taken into consideration, is that they contain the only kinetic coefficient $\overline{\mathrm{K}}_{ij}$ – the fact that considerably facilitates the investigation of transfer process kinetics.

It is worth noticing for the sake of justice that the possibility to transform kinetic equations (4.4.1) into diagonal form (14.1.5) containing the only motive force does not contradict TIP according to which the only thing necessary and sufficient for that is the linearity of laws (4.4.1) and the symmetry of phenomenological coefficient matrix therein (S. De Groot, P. Mazur, 1964). However, this procedure provided in TIP by the linear transformation of flows and forces does not advantage at all since it does not reduce the number of the independent phenomenological coefficients L_{ij} in the initial equations and does not remove the constraints intrinsic for linear TIP. Unlike TIP, thermodynamics allows to directly find the generalized form of the Fourier's, Ohm's, Darcy's, Fick's and Newton's equations by substituting the forces therein for the more general (resultant) motive force $\mathbf{F}_i$ or $\mathbf{X}_i$.

The existing of such forces assumes they have the components $\mathbf{F}_{ij} = \Theta_{\text{j}}\mathbf{X}_{\text{ij}}$ as it takes place in the anisotropic heat conduction and electric conduction equations. Therefore laws (14.1.5) may be written in the form:

$$\mathbf{J}_i = K_i\,(\mathbf{F}_j)\,\Sigma_i\,\mathbf{F}_{ij}\,, (i, j = 1, 2, ..., n). \qquad (14.1.6)$$

It is a matter of no small importance that the components $\mathbf{F}_{ij}$ of the resultant force $\mathbf{F}_j$ in equation (14.1.6) have the same dimensionality and unitary physical meaning of force in its traditional (Newtonian) conception. This allows their summing in any assortment as applied to phenomena of various nature and, thus, finding a resultant force for various poly-variant systems. Naturally, such “diagonal” laws may be transformed to their initial (matrix) form (4.4.1) by placing the coefficients $K_i(\mathbf{F}_j)$ inside the sum sign and substituting the product Θ_i $K_i(\mathbf{F}_j)$ for the coefficient L_{ij}. The “phenomenological” coefficients L_{ij} thus obtained will naturally be any more neither pure kinetic nor pure thermodynamic values, which is particularly emphasized in TIP (S. De Groot, P. Mazur, 1964). However, at such an “inverse” transformation the possibility will be lost to investigate separately the impact of thermodynamic and kinetic factors upon the transfer process, which itself is no small importance. We will see hereafter that the “diagonal” form of transfer laws (14.1.6) allows cutting the number of the pure kinetic coefficients in the transfer equations and makes superfluous the assumption of their constancy. However, the main advantage of such an approach lies in the possibility to express the superposition effects exclusively in terms of thermodynamic variables and to give them a simpler interpretation as a result of the cross compensation between the non-matching components of the resultant force. Furthermore, with the resultant motive force of a transfer process found, the impact of kinetic and thermodynamic factors upon the process may be separately investigated in a number of cases.

14.2. Superposition Effects as Found from Partial Equilibrium Conditions

Macro-processes in complex (poly-variant) physicochemical, biological, ecological, etc. systems having many degrees of freedom can practically never cease simultaneously for all degrees of freedom intrinsic to them. Usually first comes equilibrium of a one (i^{th}) kind characterized by ceasing the i^{th} process followed by equilibrium of the j^{th} kind and so on. The state characterized by ceasing a part of processes is often termed “incomplete”, “current” or “intermediate” equilibrium. We will term it “partial equilibrium of the i^{th} kind”, which will allow specializing its type (thermal, baric, diffusive, electrical, etc.). Such is the state of mechanical (more definitely – baric) equilibrium occurring well earlier than other thermodynamic processes and characterized by no cubic strain of subsystems or the system as a whole[1)], as well as thermal equilibrium in systems with a slower diffusive process taking place. Unlike the stationary state of the k^{th} order, where external forces maintain the invariability of parameters in time, partial equilibrium does not demand external forces to be applied and the parameters in this state are variable.

The notion of stationary state order is known to have been introduced into practice after I. Prigogine proved (1960) a theorem reading, "minimal generation of entropy corresponds to a state where the flows $\mathbf{J}_j$ associated with the non-fixed forces $\mathbf{X}_j$ disappear". If in a system described by n independent forces $\mathbf{X}_i$ (i =1,2,…, n) k of them are maintained constant (with the help of whatever external effects), such a state is termed the stationary state of the k^{th} order. According to this definition, when the forces $\mathbf{X}_j$ numbered k+1, k+2, etc. are not fixed, the flows $\mathbf{J}_j$ matching them disappear, and the system passes spontaneously to a stationary state of less order (with less entropy generation) subsequently until it reaches the zeroth-order stationary state, viz. equilibrium (with the zeroth entropy generation). Thereupon all superposition effects arising in the system with disappearance of whatever i^{th} flow $\mathbf{J}_i$ started to be termed stationary effects. Their formal difference from equilibrium conditions is that there are the phenomenological coefficients L_{ij} presenting in their analytical expressions, whereas the classic equilibrium conditions are expressed exclusively in terms of thermodynamic variables.

It is easy to understand why the coefficients L_{ij} appear at the stationary state conditions if to find them from Onsager's phenomenological laws (4.1.6). For the simplest case with two flows $\mathbf{J}_i$ and $\mathbf{J}_i$ these equations are:

$$\mathbf{J}_i = L_{ij}\,\mathbf{X}_i + L_{jj}\,\mathbf{X}_j, \qquad (14.2.1)$$

$$\mathbf{J}_i = L_{ji}\,\mathbf{X}_i + L_{jj}\,\mathbf{X}_j\,. \qquad (14.2.2)$$

From (14.2.2.) it follows, in particular, that for the state with $\mathbf{J}_i = 0$ the stationary effect is expressed by the relationship:

$$(\mathbf{X}_j / \mathbf{X}_i)_{\text{ст}} = -\,L_{ij} / L_{jj}\,. \qquad (14.2.3)$$

[1)] Such specialization is needed to distinguish it from the equilibrium inside a liquid flow with layers moving with the same velocity (without momentum interchange), which refers to the mechanical equilibrium category, too.

As follows from (14.2.3), the multiple superposition effects for different-kind processes are expressed in TIP via empirical coefficients depending on kinetic factors which value, unlike the thermodynamic parameters, are not known beforehand. Therefore TIP is unable to predict value of these effects. However, even more important is the fact that for isolated systems, bio-systems, oscillatory processes, media chemically reacting with reactions simultaneously running, etc., non-stationary states are inherent. The existing stationary TIP is inapplicable to such systems. This forces to search for other methods of investigating the superposition effects therein arising. Such are the methods based on the partial equilibrium conditions, which may be as well found for systems non-stationary in whole. These methods are based on the phenomenological laws represented in "diagonal" form (15.1.5). It follows from these equations that the i^{th} kind process ceases ($\mathbf{J}_i = 0$) when the components $\mathbf{F}_{ij}$ of the resultant force $\mathbf{F}_i$ mutually compensate each other:

$$\mathbf{F}_i = \Sigma_j \mathbf{F}_{ij} = 0, \qquad (14.2.4)$$

In the particular case of $j = 1,2$ $\mathbf{F}_i = \Theta_j \mathbf{X}_j + \Theta_j \mathbf{X}_j = 0$, then we obtain:

$$\mathbf{F}_i = \Theta_j \mathbf{X}_j + \Theta_j \mathbf{X}_j = 0, \qquad (14.2.5)$$

which gives

$$(\mathbf{X}_j / \mathbf{X}_i)_{\text{ст}} = - \Theta_j / \Theta_j \, . \qquad (14.2.6)$$

As will be shown hereafter, such a structure is attributed to unexceptionally all superposition effects described within thermodynamics. These relationships do not contain anymore the kinetic coefficients and, therefore, refer to the partial equilibrium conditions as if equilibrium in the field of centrifugal forces or the gravity field. The possibility of investigating non-stationary processes substantially extends the TIP applicability.

11.2. Value of Superposition Effects as Predicted from Known Thermodynamic Parameters

Characteristic features of the method proposed may be conveniently considered for a rather general class of phenomena involving diffusive mixing of the k^{th} substance in a closed heterogeneous system with invariable volume. In this continuous system under consideration, along with the external heat exchange process, the internal processes of thermal conduction, electric conduction and diffusion may also run. Let us specifically consider the diffusion of the k^{th} independent component within such a system. The diagonal form of kinetic equation for such a process hereafter termed for short as thermodynamic form looks like:

$$\mathbf{J}_k = K_k\, \Sigma_i\, \mathbf{F}_{ki} = L_k \mathbf{X}_k. \qquad (14.3.1)$$

In accordance with (4.5.6) the integral motive force of this process is understood as a difference of diffusive potential of the k^{th} component $X_k = -\Delta\zeta_k$. To expand the expression for $\mathbf{X}_k$, we will use the relation between the diffusive and chemical potentials $\zeta_k = \mu_k + Ts_{ko}$ (6.3.6). From here:

$$d\zeta_k = d\mu_k + Tds_{ko}\,. \qquad (14.3.2)$$

Considering (14.3.2) with the expression of exact differential of the chemical potential p,T,c_ℓ :

$$d\mu_k = \Sigma_k(\partial\mu_k/\partial c_\ell)dc_\ell - s_k dT + \upsilon_k dp, \qquad (14.3.3)$$

gives that at p,T = const the concentration relationship of the diffusive potential coincides with the similar relationship of the chemical potential, $d\zeta_k = d\mu_k$, since $\underline{s}_{ko} = \underline{s}_{ko}(p,T)$:

$$[d\zeta_k]_{p,T} = [d\mu_k\,]_{p,T} = \Sigma_k\, \mu_{k\ell}\, dc_\ell\,, \qquad (14.3.4)$$

where $\mu_{k\ell}$ – abridged symbol for the derivative $\partial\mu_k/\partial c_\ell$. Due to this in the general case:

$$d\zeta_k = d\zeta_k = \Sigma_k\, \mu_{k\ell}\, dc_\ell - (s_k - s_{ko})dT + \upsilon_k\, dp\,. \qquad (14.3.5)$$

From here the extended expression of resultant diffusion motive force ensues:

$$\mathbf{F}_k = -\,[\Sigma_k\, \mu_{k\ell}\nabla c_\ell + (s_k - s_{ko})\nabla T - \upsilon_k\nabla p]\ . \qquad (14.3.6)$$

Here $\mathbf{F}_{k\ell} = \Sigma_k\mu_{k\ell}\nabla c_\ell$ – component of the resultant force $\mathbf{F}_k$ responsible for usual (concentration) diffusion; $\mathbf{F}_{kT} = (s_{ko} - s_k)\nabla T$ – component responsible for thermal diffusion (substance transfer due to temperature gradient); $\mathbf{F}_{kp} = \upsilon_k\nabla p$ – component responsible for pressure diffusion (substance transfer due to pressure diffusion).

Thus the kinetic equation of diffusion in extended form is:

$$\mathbf{J}_k = K_k\, [\Sigma_k\, \mu_{k\ell}\nabla c_\ell + (s_{ko} - s_k)\nabla T + \upsilon_k\nabla p]\ . \qquad (14.3.7)$$

Let us consider for example the Soret effect – a concentration gradient ∇c_k arising in a binary mixture being in mechanical equilibrium ($\nabla p = 0$), where a temperature gradient ∇T has been created. This phenomenon means the absence of balance between the components $\mathbf{F}_{kT}$ and $\mathbf{F}_{kp}$ of the resultant force $\mathbf{F}_k$, which causes a flow of the independent k^{th} component. When partial equilibrium occurs ($\mathbf{J}_k = 0$), the expression for stationary Soret effect directly follows from (14.3.7):

$$(\nabla c_k/\nabla T)_{\text{ст}} = -\,q_k^*/T\mu_{kk}\ , \qquad (14.3.8)$$

where $q_k^* = T(s_k - s_{ko})$ – the so-called heat of k^{th} component transfer; $\mu_{kk} = (\partial\mu_k/\partial c_k)$. The expression reciprocal to the above one:

$$(\nabla T/\nabla c_k)_{\text{st}} = -\ T\mu_{kk}/q_k^* \qquad (14.3.9)$$

characterizes the stationary Dufour effect (temperature difference arising as a result of component diffusion).

Similarly from (14.3.6) the so-called thermo-mechanical effects in continuums may be predicted as showing in a gas or liquid flow arising under the temperature difference. One of them is Knudsen effect arising in vessels with initially equal ideal gas pressure after communicating them with a capillary tube. The gas overflow ceasing, stationary temperature and pressure differences set in in the vessels (in the capillary – temperature and pressure gradients). Relation between them (stationary Khudsen effect) may be determined directly from (14.3.6). In this case $\nabla c_k = 0$, and due to mutual compensation of the last two terms it follows that

$$(\nabla p/\nabla T)_{st} = -\,q_k^*/T\upsilon. \qquad (14.3.10)$$

This effect is explained from thermodynamics by a distinction between the entropy s_k in the pores or capillaries of the membrane and its value beyond them (in the vessels) s_{ko}. This is most evident from Knudsen effect (1910) when the pressure difference Δp disappears with increasing the diameter of the capillary or the width of the gap connecting the vessels with gas of different temperature (Haase, 1967). In this case the invariably negative value of the transfer heat q_k^* in Knudsen effect evidences that the entropy s_k of the gas transferred thru the capillary system is less than the entropy s_{ko} of the same gas in its "free" state. This is natural since the gas transferred thru the capillaries lacks a part of the degrees of freedom in mechanical motion of molecules (i.e. it is more ordered).

In the same way the sedimentation effect may be predicted widely used at the uranium enrichment in centrifuges. The component separation is caused therein by a pressure gradient ∇p arising in binary solutions as generated by centrifugal forces. In the state of sedimentation equilibrium in the centrifugal field the first and the third terms of expression (14.3.6) are mutually compensated at $\nabla T = 0$, which directly gives the stationary effect expressed as:

$$(\nabla c_k/\nabla p)_{\mathrm{st}} = -\,\upsilon_k\,/\mu_{kk}\,. \qquad (14.3.11)$$

It is significant that this result has been obtained within the linear theory of irreversible processes also from the equilibrium conditions, whereas Soret, Dufour, Knudssen, etc. effects – from the stationary state conditions. This tells to the TIP inconsistency that evidences also from the fact that the said effects maintain their character also after the independence of both flows (heat and substance) has been provided.

Thus the method proposed allows predicting the value of the superposition effects in the states of partial equilibrium from the thermodynamic parameters Θ_{j} and Θ_{j} known (V. Etkin, 1999) or finding the hard-to-measure thermodynamic parameters of the s_k, $\mu_{k\ell}$, etc. type as based on measuring the stationary superposition effects of the (14.2.6) type.

14.4. Simplification of Phenomenological Laws without Onsager's Reciprocal Relations Applied

As shown in Chapter 4, the application of TIP to investigate the effects of superposition (interaction) of irreversible processes having various nature starts off with setting up the balance equation for mass, momentum, charge, angular momentum and energy in order to subsequently identify therein the terms defining the entropy rise rate in a system under investigation and to find from them the cofactors that may be interpreted as the generalized rates of irreversible processes (the flows $\mathbf{J}_j$) and their motive forces $\mathbf{X}_i$. To set up such equations, thorough knowledge of the entire complex of scientific disciplines is required, which equations contain (unlike thermodynamics) time as a physical parameter and which processes effect the entropy generation. Then based on these balance equations a similar entropy equation of the (4.3.1) and (4.3.2) type is formulated followed by identifying therein terms associated with the entropy "generation" and dividing them into flows and forces. Such a division into cofactors may be implemented by different ways, which supposes certain arbitrariness in choosing flows and thermodynamic forces, their dimensionality and the meaning associated. Next step is to set up Onsager's kinetic equations (phenomenological laws) (4.1.6) for particular processes under investigation. These equations are then considered jointly with Onsager's symmetry conditions (4.1.7) or (4.1.8) which interrelate the flows $\mathbf{J}_i$ and $\mathbf{J}_j$. And only after that expressions of the so-called "stationary superposition effects" are determined as corresponding to disappearance of one of the flows $\mathbf{J}_i$ or $\mathbf{J}_i$ with the non-equilibrium state of the system maintained.

Thus the determination of the TIP-based superposition effects is a quite complicated multi-stage problem involving profound knowledge of many special disciplines. However, this but adds to the proposed method that allows finding the shortest way to solution to the problem. This becomes possible due to the fact thermodynamic equations of the (2.5.9) type already contain time, flows and thermodynamic forces and, therefore, do not need a clumsy form of balance equations for mass, charge, momentum, energy and entropy. Besides, thermodynamics eliminates whatever arbitrariness in choosing motive forces and generalized rates of any (both scalar and vector) processes – their meaning and dimensionality are unambiguously defined by the character of the coordinate Θ_i as a quantitative measure of the particular energy form carrier. In this case, according to (2.5.8), the thermodynamic forces are expressed exclusively in terms of the negative gradients of the generalized potential associated with the Θ_i, while the flows $\mathbf{J}_i$ or $\mathbf{j}_i$ are the product of these values and their transfer velocity under the action of the forces $\mathbf{X}_i$.

Furthermore, thermodynamics considerably simplifies the phenomenological laws reducing them to the so-called "diagonal form" (14.1.5) which contains minimal number of the kinetic coefficients $\bar{\mathrm{K}}_{\mathrm{ij}}$. These laws are based on the statement proved in the previous paragraph and reading that for each independent process the only (resultant) force exists which disappearance ceases the process of this kind.

Let us consider for example the equations of multi-component isobaric-isothermal diffusion, for which L.Onsager proposed (1945) the phenomenological laws of the kind:

$$\mathbf{j}_i = -\Sigma_j L_{ij} \nabla\mu_j \, , (i, j = 1, 2, \ldots, K-1). \tag{14.4.1}$$

This equation assumes that the flow $\mathbf{j}_k$ of any of the K–1 independent (emphasis added) components of a system, nevertheless, depends on all thermodynamic forces acting in the system, which are, in the case of isobaric-isothermal diffusion, identified with the negative gradients of chemical potential of each of such j^{th} components μ_{j}. The additional (non-diagonal) terms $i \neq j$ of the first sum of this expression were introduced by L. Onsager to allow for the interrelation between flows, which he used to explain the "ascending diffusion", viz. transfer of a substance in the direction of its concentration increasing.

Since the chemical potential of any of the j^{th} substances is a function of temperature T, pressure p and concentration c_k of the independent k^{th} components, its differential $d\mu_{\mathrm{j}}$ at p,T = const features exclusively its dependence on concentration, which may be expressed as:

$$d\mu_j = \Sigma_k (\partial\mu_j/\partial c_k) dc_k = \Sigma_k \mu_{jk} dc_k \, , \tag{14.4.2}$$

where μ_{jk} – abridged symbol for the derivative $\partial\mu_j/\partial c_k$. Therefore equation (14.4.1) has actually the form:

$$\mathbf{j}_i = -\Sigma_j L_{ij} \Sigma_k \mu_{jk} \nabla c_k \, , (i, j, k = 1, 2, \ldots, K-1) \tag{14.4.3}$$

i.e. contains a double sum of terms, which sharply complicates determining the already hard-to-determine cross phenomenological coefficients. The formal simplification of these equations as

$$\mathbf{j}_i = -\Sigma_j D'_{ik} \nabla c_k\,,\ (i, j, k = 1, 2, \ldots, K\text{–}1) \qquad (11.4.4)$$

by introducing the diffusion coefficients

$$D'_{ik} = \Sigma_k L_{ij} \mu_{jk} \qquad (14.4.5)$$

does not matter since keeps invariable the former number of the kinetic L_{ij} and thermodynamic μ_{jk} factors influencing the diffusion of the i^{th} component. The double sum in (14.4.3) with the number of summands $K(K–1)$ results in an extremely complex relationship between the said values and makes the statement of the problem of finding the non-diagonal diffusion coefficients $D'_{i\ell}$ in metals and alloys with the existing methods of experimental determining the fields of impurity concentration (including the X-ray diffraction analysis) mathematically incorrect (Krishtal, Volkov, 1985). This forces investigators to apply a number of assumptions. When investigating the diffusion in metals, both sums in (14.4.3) are most often neglected and the so-called Birchenall-Mehl approximation is used:

$$\mathbf{j}_i = -(L_{ij} R_\mu T/a_i)\, \nabla a_i = -D_i^* \nabla a_i\,, \qquad (14.4.6)$$

or Darken approximation

$$\mathbf{j}_i = -D_i^* (\partial a_i/\partial c_i) \nabla c_i = -D_i \nabla c_i\,, \qquad (14.4.7)$$

wherein the chemical potential $\mu_i = \mu_i^{\text{o}} + R_\mu T \ln a_i$ is represented by a known way in terms of its standard value $\mu_{\text{k}}^{\text{o}}$ and the activity a_i of this component by Lewis, while the dependence of the i^{th} diffusive flow on the concentration gradients of other components is allowed for indirectly in terms of the “true” $D_i = L_{ii} R_\mu T/a_i$ or “effective” $D_i = D_i^*(\partial a_i/\partial c_i)$ diffusion coefficients with the help of a number of empirical or semi-empirical relationships (M. Krishtal, 1972). Without these additional relationships equations (14.4.6) and (14.4.7) can not describe the ascendant diffusion phenomenon, concentration discontinuities on the welding border, bulk effects like Kirkendal effect (replacement of diffusion pair border), etc.

Therefore it is a matter of interest to compare the simplifying assumptions proposed with those ensuing from thermodynamics.

Let us consider for example an arbitrary discontinuous system like the diffusive welding pair on Fig.14.1). Such a pair is formed as a result of vacuum diffusion welding of two plates having different compositions. One of the subsystems (left-hand) is a three-component system containing, along with iron (Fe), also chromium (Cr) and carbon (C), while the other (right-hand) – iron (Fe) and carbon (C). The dots on the figure denote the experimentally found atomic concentrations of the components.

As follows from Fig.14.1, in the course of high-temperature annealing of the system under consideration (Fe + Cr + C) – (Fe + C) carbon transfer is observed in the direction of carbon concentration increase (carbon ascending diffusion) leading to a carbon concentration discontinuity in the diffusion welding area with a thickness of δ. This discontinuity can not be anymore explained by the generation of the so-called “dissipative structure” (according to the Prigogine’s terminology) supported by the irreversible processes running in the system since in this case the system in whole is closed and none of the thermodynamic forces $-\nabla c_k$ is artificially maintained therein. This means that the steady-state concentration distribution among the substances in the system refers indeed to partial equilibrium.

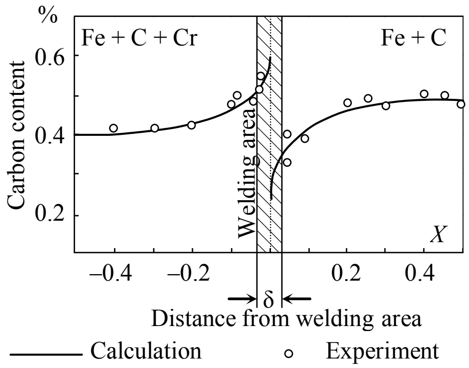

Fig.14-1. Carbon Ascending Diffusion in Alloys

Let us apply the thermodynamic approach to describe the phenomenon of ascending diffusion. From the positions of thermodynamics there is the only motive force existing for a flow of any independent component $\mathbf{j}_i$, which engenders this flow with all the associated superposition effects. For the isobaric-isothermal diffusion in continuums according to (14.3.5) the negative gradient of the diffusion potential ζ_k is the resultant force of the process. However, since $\zeta_k = \mu_k + Ts_{ko} - p\upsilon_{ko}$, then at p,T = const the diffusion and the chemical potentials have the same dependence on concentration because $[d\zeta_k]_{p,T} = [d\mu_k]_{p,T}$. Therefore the negative gradient of the chemical potential of the i^{th} component may still remain the motive force of the concentration diffusion, i.e. $\mathbf{X}_D = -\nabla\mu_i$. Since this potential is the function of concentrations of all independent system components, the Fick's generalized diffusion law takes the form:

$$\mathbf{j}_i = -L_{ii}\Sigma_k\,\mu_{ik}\nabla c_k = -\Sigma_k\,D_{ik}\nabla c_k, \tag{14.4.8}$$

where $D_{ik} = L_{ii}\mu_{ik}$ – generalized diffusion coefficients. This expression features much simpler form of diffusion coefficients, which consequences allow a direct experimental check with the up-to-date means of investigating diffusion in metals. One of such consequences is the simple relationship between the thermodynamic μ_{ik} and kinetic L_{ij} factors of diffusion:

$$D_{ii}/\mu_{ii} = D_{ik}/\mu_{ik}\,. \tag{14.4.9}$$

The relationship of such a kind was set up earlier in Darken approximation (Brown, Kirkaldy, 1969). Let us use now this condition of the simultaneously disappeared flow $\mathbf{j}_i$ and its thermodynamic force $\mathbf{X}_D$. This condition should be referred to the partial (incomplete) equilibrium state since it occurs for components relatively fast diffusing with the redistribution of other components (in this case – chromium) going on. This state features, as experiment shows (Fig.14.1), a carbon concentration discontinuity on the welding border. It may be more conveniently described if changing to the integral form of the diffusion motive force $\mathbf{X}_D^c = -\Delta\mu_k = \Sigma_k\,\bar{\mu}_{ik}\,\Delta c_k$, where $\bar{\mu}_{ik}$ – mean value of the coefficient μ_{ik}. Then from expression (14.4.9) it may be found:

$$\Sigma_k\,\bar{\mu}_{ik}\,\Delta c_k = 0\,. \tag{14.4.10}$$

In the particular case of three-component systems with the third component slowly moving:

$$\bar{D}_{23} = \bar{D}_{22}\ (c_2' - c_2'')/(c_3'' - c_3')\,, \tag{14.4.11}$$

where c_2' , c_2'' , c_3' , c_3'' – impurity concentrations on both sides of the welding border.

This relationship evidences the generation of the concentration discontinuities ($c_2' - c_2''$) in the fast diffusing substance when its equilibrium distribution sets in, which is experimentally confirmed. One more relationship for the diffusion pair under consideration may be obtained based on the expression:

$$\Delta\mu_i = -\Sigma_k\, \overline{\mu}_{ik}\, \Delta c_k\ . \qquad (14.4.12)$$

When comparing (11.4.12) with the similar expression $\Delta\mu_i = -\ \overline{\mu}_{ik}\, \Delta c_i$ for a binary system and using relationship (14.4.9) one can find an expression for the so-called “distribution coefficient” of the i^{th} component c_i'/c_i'', which is the relationship between its concentrations in the binary system and that under investigation:

$$æ_i = 1 + \Sigma_k\, \chi_{ik}\, c_k\ , \qquad (11.4.13)$$

where $\chi_{ik} = D_{ik}/D_{ii}c_k$ – the so-called parameter of cross-impact between the i^{th} and the k^{th} components.

This expression differs from a number of empirical relationships such as Wagner formula (Krishtal, 1972) and is a matter of principal interest since directly relates equilibrium concentrations and the hard-to-measure diffusion coefficients D_{ik} (V. Etkin, 1994). To check it, let us apply to the amply available data on the carbon distribution in the system (Fe + 6.5%Cr + 0.4%C) – (Fe + 0.49%C) after the 5-hour annealing at a temperature of 1,000^{0}C (see Table (14.1):

Table 11.1

Carbon Distribution Coefficient in Austenite

Content of components, atomic percentage			Experiment, atomic percentage				Calculation
C,		Cr,	[1]	[2]	[3]	Mean	
Iron	Alloy	Alloy					
2.28	7.81	6.38	0.35	0.57	0.38	0.44	0.47
	4.76	6.58	0.52	0.46	0.41	0.46	0.44
1.15	2.85	6.70	0.43	0.41	0.40	0.41	0.42
0.74	1.64	6.78	0.47	0.38	0.41	0.42	0.41

The *C* (second component) – *Cr* (third component) cross-impact coefficient remains practically constant within the given concentration range and equal to $\chi_{23} = -10{,}9$ (Chipman, Bruch, 1968). The calculated f values have been found from expression (11.4.11) and compared in this table with the data from three independent experiments (M. Krishtal, 1972; Chipman, Burch, 1968; Shenk, Kaiser, 1960). As follows from the table, the calculated and mean measured data complies quite satisfactorily. It is worth noting that this result was earlier obtained by balancing the activities (supposing the activities a_k' and a_i'' being equal in both parts of the pair at partial equilibrium) and confirmed experimentally on a number of metallic alloys Fe-based [1], which is illustrated by Fig.11.1 (Krishtal, 1972).

As another example, let us consider a three-component system Fe + Si + Cr that is a matter of not only theoretical, but also practical interest in the context of siliconizing of chromium steels. Diffusion pairs (Fe + Si) – (Fe + Cr) with different content of silicon and chromium were investigated. Experimental value æ was determined as the ratio of the Si concentrations in iron and alloy; the ratio D_{23}/D_{22} was found from expression (14.4.10). The calculation and experimental data is shown in Table 14.2.

Table 14.2

Calculated and Experimental Values of Silicon Distribution Coefficient in Welded Diffusion Pairs

Content		Ratio	Parameter	Distribution coefficient	
Si, %	Cr, %	D_{23}/D_{22}	χ_{23}	Calculation	Experiment
1.0	6.7	0.03	3.00	1.20	1.30
2.0	6.7	0.07	3.50	1.20	1.2
3.0	6.7	0.11	3.66	1.26	1.33
4.0	6.7	0.15	3.75	1.26	1.33
3.0	1.0	0.10	3.33	1.04	1.15

---

[1] It is easy to note that the activities balancing method proceeds from the same assumptions as thermodynamics

It should be emphasized that theoretical calculations of such systems forming substitution solutions are especially complicated; therefore the possibility to find "cross" diffusion coefficients featuring their interference is a matter of no small consequence.

The data of the above table evidences quite exact compliance between the experimental and calculated æ values. The minor systematic deviation of the calculated æ values from the experimental ones may be explained by neglecting the c_3' value calculated from (14.4.11). Thus the data of the considered experiments confirms that the diagonal form of the multi-component diffusion laws includes the whole information of superposition effects despite it is much simpler than that Onsager postulated. Thereby the conclusion of thermodynamics is once again confirmed that the motive forces in non-related irreversible processes are unique (Etkin, 1989) and the Onsage's postulate should be superseded for such processes by a statement each flow depends on only all components of the resultant thermodynamic force. Since all summands of this force $\mathbf{X}_i$ have the same tensor order, such a revision of the physical concept of Onsager's postulate intrinsically corresponds to Curie principle that excludes the interrelation between phenomena of different (odd) tensor order. This is such (resultant) force that should have been named thermodynamic since the fact itself of its existence, as well as its particular form for each of the independent processes is defined by the basic equation of thermodynamics. Such a force found allows avoiding the "over-determination" of the flow given in expression (14.4.2) as a function of thermodynamic forces and retaining the simple form for known laws of thermal conduction, electric conduction, diffusion, filtration, momentum transfer at their generalization to the case of superposition of different-kind phenomena.

14.5. Investigation of Membrane Processes with the Reciprocal Relations Violated

The Onsager's symmetry conditions $L_{ij} = L_{ji}$ or Onsager-Cazimir's anti-symmetry conditions $L_{ij} = -L_{ji}$ are known to be violated (S. De Groot, P. Mazur, 1974) providing the coefficients L_{ij} and L_{ji} are inconstant, i.e. depend on the parameters of the system, in particular, the thermodynamic forces $\mathbf{X}_i$ and $\mathbf{X}_j$. This fact significantly restricts the existing TIP applicability since the existence of such dependence is doubtless. The situation changes when the transfer equations are represented in diagonal form (11.1.6), while the superposition effects are determined from the partial equilibrium conditions. In this case, as shown hereinbefore, the kinetic coefficients are cancelled out and the superposition effects are found from the condition of mutual compensation of the resultant force components without appeal for the reciprocity relationships to be used.

Let us show this by a quite general example of multi-component systems divided into two subsystems with a porous partition, capillary, valve, finite-thickness membrane, etc (Fig.14.2).

The partition has generally finite dimensions and is, therefore, considered as one of the subsystems within such a "combined" (discontinuous-continuous) system. The system in whole is a spatially heterogeneous medium featuring temperatures T, pressures p, concentrations c_k, etc. continuously varying across the thickness of the membrane, whereas distribution of temperatures, pressures and concentrations outside the membrane being practically homogeneous (intrinsically equilibrium) (respectively, T', p', c_k' and T'', p'', c_k'', etc.).

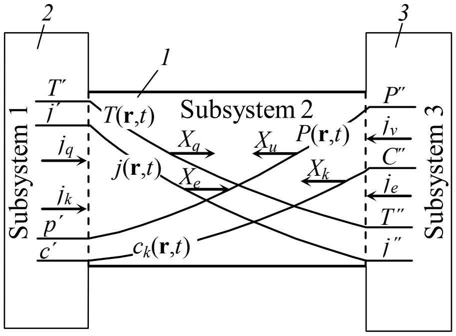

Fig.14.2. Combined (Discontinuous-Continuous) System

1 – membrane (continuum)

2, 3 – reservoirs of heat and substance

The effects arising in such a system is more conveniently to be considered starting off with the simplest case of a single-component medium ($c_k' = c_k'' =$, $\upsilon_k = \upsilon$) having intrinsically the same pressure on both sides of the porous partition ($p' = p''$). With the temperature difference ($\Delta T \neq 0$) generated in such a system a gas or liquid flow across the partition arises resulting in pressure difference. This phenomenon was first described by Feddersen (1873), who observed a flow of air across a plaster wall in the direction toward the higher temperature and termed it thermo-diffusion. This phenomenon is presently known as thermo-osmosis. The thermo-osmosis ceases with both components of the osmotic force, $F_{kT} = (s_{ko} - s_k)\Delta T$ and $F_{kp} = -\upsilon_k \Delta p$, mutually balanced. From here, given the relationship $(s_{ko} - s_k) = q_k^*/T$ (where q_k^* – the so-called transfer heat of the k^{th} component), a known expression of Feddersen stationary effect directly follows (Groot, 1956):

$$(\Delta p/\Delta T)_{\mathrm{st}} = -q_k^*/T\upsilon_k\,. \tag{14.5.1}$$

There is the inverse phenomenon also known, viz. a temperature difference arising across the two sides of a partition with air or other gas being forced thru it. Both these effects have the same nature with Knudsen effect (1910), as well as with Allen - Jones effect (1938) in liquid helium II (fountain effect) consisting in overflow of helium out from a bulb closed up with a porous cork under a minor heating (Haase, 1967). Assuming for this case (London, 1938) that the superfluid component of helium II passing thru the porous cork or capillary has zero entropy ($s_{k\mathrm{o}} = 0$) expression (14.5.1) becomes:

$$(\Delta p/\Delta T)_{\mathrm{st}} = s_k/\upsilon_k\,, \tag{14.5.2}$$

which corresponds to the result London earlier obtained by the "pseudo-thermostatic" way. There is the inverse phenomenon also known, viz. a temperature difference arising with a pressure difference generated across the two sides of a partition, which was termed as mechanocaloric effect (Daunt-Mendelson).

In isothermal systems ($\Delta T = 0$) under a pressure difference Δp generated across a membrane the phenomenon of reverse osmosis arises, viz. binary solution separation with extracting the k^{th} component (usually solvent) therefrom. This phenomenon is being applied in ever growing scale in water purification units. The stationary concentration difference of the k^{th} component arising therein is described as:

$$(\Delta c_k/\Delta p)_{\mathrm{st}} = -\upsilon_k/\mu_{kk}\,. \tag{14.5.3}$$

There is the inverse phenomenon also known, viz. an osmotic pressure difference (osmotic pressure) Δp arising at redistribution of the k^{th} component, which plays an important role in biological systems. Both these effects do not include the transfer heat and are reversible.

Now let us consider even more complicated case when the membrane is permeable (though in different degree) for both of the components. There are the flows of the 1st and 2nd components $\mathbf{J}_1$ and $\mathbf{J}_2$ arising in such a system, for which the thermodynamic transfer laws, due to $\Delta c_2 = - \Delta c_1$, take the form:

$$\mathbf{J}_1 = - L_1 \left[\Sigma_k \mu_{11} \Delta c_1 + (s_1 - s_{10}) \Delta T + \upsilon_1 \Delta p\right] ; \tag{14.5.4}$$

$$\mathbf{J}_2 = - L_2 \left[\Sigma_k \mu_{21} \Delta c_1 + (s_2 - s_{20}) \Delta T + \upsilon_2 \Delta p\right] . \tag{14.5.5}$$

The separation of a mixture in such systems into components due to a temperature difference maintained is sometimes termed as thermo-effusion to distinguish this phenomenon from the thermo-diffusion (redistribution of components in the absence of membranes and convective gas or liquid flow (S. De Groot, 1956). Given the interrelation of the chemical potential derivatives $\mu_{21} = - (c_1/c_2)\mu_{11}$ ensuing from Gibbs-Duhem relationship at p,T = const and solving the set of equations (14.5.4)…(14.5.5) for the Δc_1 and ΔT the expression of stationary thermo-effusive effect may be found:

$$(\Delta c_1/\Delta T)_{\text{ст}} = (\upsilon_1 q_2^* - \upsilon_2 q_1^*)/T\upsilon\mu_{11} . \tag{14.5.6}$$

Similarly solving the same set of equations for Δp and ΔT and given $(s_{10} - s_1) = q_1^*$; $(s_{20} - s_2) = q_2^*$ the expression for thermo-mechanical effect may be found (R. Haase, 1967):

$$(\Delta p/\Delta T)_{\text{st}} = - (c_1 q_1^* + c_2 q_2^*)/\upsilon , \tag{14.5.7}$$

where $\upsilon = c_1\upsilon_1 + c_2\upsilon_2$..

All these results comply with those obtained within the frames of TIP. However, there was no need to apply now to the Onsager-Cazimir's reciprocity relationships and assume the linearity of phenomenological laws, as well as the constancy of phenomenological coefficients (their independence on the thermostatic parameters). On the contrary, it is quite evident that the processes in the system considered are non-linear since the coefficients of thermal conduction, electric conduction, diffusion, filtration and viscous friction in Fourier's, Ohm's, Fick's, Darcy's and Newtons's empirical laws depend on temperature, pressure, composition and number of other parameters varying across the thickness of the membrane. This violates their constancy requirement which in the Onsager's theory bears the principal character and constitutes a substantial part of his law (S. De Groot, P. Mazur, 1964). In fact the forces X_i in his theory were determined by a deviation of the system parameters ψ_i (temperature, pressure, component concentrations, etc.) from their equilibrium values and were, therefore, functions of these parameters. In such a case the dependence of the coefficients L_{ij} on these parameters implies their dependence on also the forces X_j, i.e. the non-linearity of phenomenological laws (5.1.6). This violates the conditions under which the statistic-mechanical substantiation may be applied to symmetry of phenomenological coefficients matrix as used by Onsager and, thus, excludes the possibility of using these coefficients in the membrane processes. It is even more important that the method proposed does not demand the application of the Onsager's relationships violated in such systems. The analytic expressions for the superposition effects herein obtained do not depend on the fact whether the phenomenological laws (see 5.1.7) are linear or not and whether the Onsager-Cazimir's reciprocity relationships are observed or not therein. This means that the said effects bear a more fundamental character.

The fact attracts attention as well that all of the said effects reach their peak values at stationary states when one of the flows (mostly the flow of the k^{th} component) disappears and therefore just can not superimpose on the remainder flows. This once again evidences the inconsistency of the TIP-associated interpretation of these effects as a result of superposition (interaction) of the flows. As appears on close inspection, these effects arise due to superposition of motive forces, i.e. in exactly the same way as this occurs in mechanics and other disciplines. The principal difference between these two interpretations is that the superposition effects in thermodynamics are functions of state, but not of process, and arise from the partial equilibrium conditions, but not from whatever order stationary state conditions.

Chapter 15

GENERALIZATION OF THE THEORY TO SYSTEMS STANDING FAR AWAY FROM EQUILIBRIUM

This chapter is dedicated to thermokinetic description and investigation of a number of interrelated non-linear transport processes based on the method offered in the previous chapter. The method basically consists in defining the superposition effects of irreversible processes from the partial equilibrium conditions. In the case of interrelated processes it is realized by using the differential reciprocity relationships allowing for the contribution of an alien force to a phenomenon under investigation and thus making such processes independent. This allows finding for each of them a resultant motive force which disappearance ceases the process. Such an approach enables the further (relative to TIP) reduction of the number of kinetic factors in these laws and the expression of the superposition effects in the same way as in Chapter 11 for independent processes.

The efficiency of the method offered and the validity of the conclusions obtained from thermodynamics will be here confirmed on a numerous experimental data.

15.1. Reciprocal Relations for Chemical Reactions

Classic thermodynamics with its laws considers only initial and final states of a chemically reacting system not touching upon kinetics of chemical reactions, i.e. the rate of the initial-to-final state transit for the system. The factors affecting this rate, (such as temperature, concentration of reagents, catalysts available, etc.) have been subject of chemical kinetics. This postulates, according to the Guldberg & Waage mass action law, that the rate of a chemical reaction is proportional to the product of reagents' concentration. Since any chemical reaction runs in both forward and backward directions, its resultant rate is defined by the difference between the rates of direct ω_r' and reverse ω_r'' reactions:

$$w_r = \omega_r' - \omega_r'' = \omega_r' \left(1 - \omega_r''/\omega_r'\right) . \qquad (15.1.1)$$

According to the detailed balance principle a reaction stops when the rate of direct reaction becomes equal to that of reverse reaction. In this case the affinity of the reaction A_r becomes equal to zero. From this it follows that

$$A_r = R_\mu T \ln (\omega_r''/\omega_r') , \qquad (15.1.2)$$

where R_μ – universal gas constant.

Considering (15.1.1) and (15.1.2) jointly the kinetic laws of chemical reactions may become exponential dependences of the type:

$$w_r = \omega_r' \, [1 - \exp (-A_r/R_\mu T)] \, . \qquad (15.1.3)$$

These equations term the Guldberg & Waage laws. The dependence of ω_r' on temperature within a quite wide range is here described by the Arrenius empirical law:

$$\omega_r = \omega_{ro} \exp (-E_a/RT) , \qquad (15.1.4)$$

where ω_{ro} – Arrenius factor; E_a – activation energy required to initiate reaction

This non-linearity of chemical reactions leads to a violation of the Omsager-Cazimir's reciprocity relationships therein with the result that the applicability of TIP to chemically reacting systems is restricted to next-to-equilibrium states. The thermodynamic substantiation of more general differential reciprocity relationships (4.5.3) offered in Chapter 4 allows overcoming this restriction. Let us consider for example the case of interrelated chemical reactions obeying the Guldberg & Waage chemical kinetics laws (15.1.3). For this let us apply to the class of ternary unimolecular reactions L. Onsager earlier considered (1931). These reactions with substances *L, M, N* may be described by two different ways: either as a two-linear-independent reaction model (R. Haase, 1967):

$$\text{L} \leftrightarrow \text{M (reaction 1);}$$

$$\text{M} \leftrightarrow \text{N (reaction 2),} \qquad (15.1.5)$$

or as a linear-dependent elementary reaction model (see Fig.15.

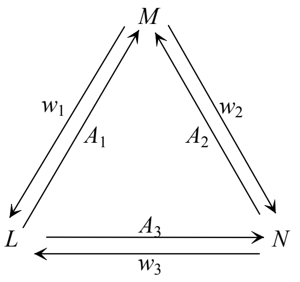

Fig. 15.1. Ternary unimolecular reaction

$$L \leftrightarrow M \quad \text{(reaction 1)},$$
$$M \leftrightarrow N \quad \text{(reaction 2)}, \qquad (15.1.6)$$
$$N \leftrightarrow L \quad \text{(reaction 3)}.$$

The first model features a purely macro-approach, where a merely general process is described with the help of mathematically independent equations. The second model describes a reaction mechanism, i.e. a real chemical conversion process (R. Haase, 1967). The above elementary reactions run with rates w_1, w_2 and w_3, respectively, being expressed, according to the Guldberg & Waage laws, by the following exponential kinetic equations:

$$w_1 = \omega_1' \, [1 - \exp(-A_1/R_\mu T)] \, ;$$
$$w_2 = \omega_2' \, [1 - \exp(-A_2/R_\mu T)]; \qquad (15.1.7)$$
$$w_3 = \omega_3' \, [1 - \exp(-A_3/R_\mu T)] \, ,$$

where ω_1' , ω_2' , ω_3' – rates of the corresponding direct reactions; A_1, A_2, A_3 – their current affinities interrelated to the Gess law as A_1 + A_2 = A_3. According to these equations the dissipation function $T\sigma_s$ for the system under consideration is:

$$T\sigma_s = w_1 A_1 + w_2 A_2 + w_3 A_3 \, . \qquad (15.1.8)$$

For the considered case the rates of the reactions and their affinities are linear-dependent (i.e. represent a linear combination of each others). At such conditions the symmetry conditions are known not to be guaranteed (De Groot, 1956). Therefore let us introduce two new linear-independent rates:

$$w_\alpha = w_1 + w_2 \, ; \, w_\beta = w_2 + w_3 \, . \qquad (15.1.9)$$

Two independent forces A_α and $A_\beta$correspond to these rates, which allows equations (15.1.7) to be transformed, subject to the invariance of the dissipation function $T\sigma_s$, to the form:

$$w_\alpha = L_{11}\,[1 - \exp(-A_\alpha/R_\mu T)] + L_{12}\,[1 - \exp(-A_\beta/R_\mu T)], \quad (15.1.10)$$

$$w_\beta = L_{21}\,[1 - \exp(-A_\alpha/R_\mu T)] + L_{22}\,[1 - \exp(-A_\beta/R_\mu T)]. \quad (15.1.11)$$

Here

$$L_{11} = \omega_1' + \omega_2';\ L_{12} = \omega_3' \exp(-A_\alpha/R_\mu T)]\ ; \qquad (15.1.12)$$

$$L_{21} = \omega_3' \exp(-A_\beta/R_\mu T)];\quad L_{22} = \omega_1' + \omega_3'\ . \qquad (15.1.13)$$

Thus a ternary reaction far from equilibrium may be described by two non-linear kinetic equations with linear-independent rates and forces. Here the coefficients ω_1', ω_2' and ω_3' being functions of temperature, pressure and concentrations of parent substances for the corresponding reaction do not depend on its affinity. In fact, according to (15.1.2) the affinity A_r of any of the r^{th} reactions is defined by the relation between the rates of direct and reverse reactions and does not depend on each of them separately. Hence chemical reactions are described by exponential kinetic equations with phenomenological coefficients independent on forces. In this case generalized reciprocity relationships (5.5.3) should be true having in our case the form:

$$\partial w_\alpha/\partial A_\beta = \partial w_\beta/\partial A_\alpha\ . \qquad (15.1.14)$$

To make sure they are valid, it is enough to differentiate expression (15.1.10) with respect to A_β, given L_{11} and L_{12} independent on A_β, and to repeat the similar operation on (15.1.11) with respect to w_β. The result will be as follows (V. Etkin, 1982):

$$\partial w_\alpha/\partial A_\beta = \partial w_\beta/\partial A_\alpha = (\omega_3'/R_\mu T)\exp(-A_3/R_\mu T). \qquad (15.1.15)$$

It can be easily seen that with approaching equilibrium, when A_1, A_2 and A_3 are simultaneously tending to zero, relationship (15.1.15) goes over into known Onsager's symmetry conditions for chemical reactions in the form:

$$L_{12} = L_{21} = \omega_3'/R_\mu T\,. \qquad (15.1.16)$$

This example shows that the generalized reciprocity relationships do not follow from the Onsager's symmetry conditions as usually considered, but, on the contrary, these conditions themselves ensue from the differential reciprocity relationships near equilibrium when the linear approximation appears to be valid.

Thus thermokinetics appears to be quite compatible with the exponential laws of Guldberg & Waage chemical kinetics, which opens up additional vistas in the thermodynamic analysis of chemical technology processes and the evolutional problems of biological and ecological systems.

15.2. Investigation of Irreversible Processes in Systems Standing far from Equilibrium

Measuring gradients of temperature, pressure, chemical, electrical, etc. potential in non-equilibrium systems divided into parts (subsystems) with membranes, capillaries, gates, etc., is practically excluded. In this case the thermodynamic transport laws have to be written down in the integral form where the thermodynamic forces are represented in terms of differentials of the potentials mentioned. Then the phenomenological coefficients K_k which are functions of thermostatic variables become implicit functions of the thermodynamic forces $\mathbf{F}_k$ since these depend now on the fields of temperatures, pressures, concentrations, etc. Such dependence makes the transport laws linear since these fields vary with variation of the forces $\mathbf{F}_k$ themselves. As shown on example of chemical reactions, the Onsager's reciprocity relationships in such systems are violated all the more the further the system stands from equilibrium. That was brought out clearly in the very thorough experiments the group of American investigators from the Oak-Ridge National Laboratory (USA) carried out to solve the problem of creating nuclear reactors with gas heat carrier for spacecrafts (Ewans, Watson, Truitt, 1963; Mason, Wendt, Bresler, 1972). A system was considered comprised of two hollows separated with a graphite membrane of medium permeability. There was substantially pure argon ($x_1 = 0.9711$) on a one side of the membrane and substantially pure helium ($x_2 = 0.9917$) on the other side. Both gases were maintained in a state with the same temperature. As a result, the counter flows $\mathbf{J}_1$ of argon and $\mathbf{J}_2$ of helium (mole/s) occurred across the membrane. The pressure differential Δp having been generated across the membrane, the filtration process superimposed on the isothermal diffusion with the result of the volumetric flux $\mathbf{J}_V$ (cm^3/s) arisen. By changing the pressure differential in value and sign a stationary state could be obtained with the volumetric flux ceased [1].

As independent flows, the investigators considered the diffusion flux $\mathbf{J}_D$ (cm^3/s) = $\mathbf{J}_1/n_1 - \mathbf{J}_2/n_2$ (where n_1, n_2 – molar concentrations of argon and helium, respectively, mole/cm^3), which does not vary with filtration due to the equality of the volumes $\mathbf{J}_1/n_1$ and $\mathbf{J}_2/n_2$ therein, and the volumetric (filtration) flux of the gas mix $\mathbf{J}_V$ (cm^3/s) $= V_\mu (\mathbf{J}_1 + \mathbf{J}_2)$, which does not vary with diffusion due to the equality of the flows $\mathbf{J}_1 = -\mathbf{J}_2$ therein (i.e. the constancy of the mole numbers in the subsystems). Diffusion motive force was adopted as the mole fraction differential for one of the system independent components (argon) $\mathbf{X}_D = -\Delta x_1$, which remained practically constant in the experiment, while filtration motive force was adopted as the total pressure differential $\mathbf{X}_V = -\nabla p$. Then the Onsager's phenomenological laws become:

$$\mathbf{j}_D = -L_{DD} \nabla x_1 - L_{DP} \nabla p , \qquad (15.2.1)$$

$$\mathbf{j}_V = -L_{PD} \nabla x_1 - L_{PP} \nabla p , \qquad (15.2.2)$$

where $\mathbf{j}_D$, $\mathbf{j}_V$ –diffusion and volumetric flux densities, respectively, cm^3/cm^2·s; L_{DD}, L_{DP} – phenomenological diffusivity (the first index "*D*" in both subscripts) resulting from diffusion and filtration (the second index "*P*") motive forces, respectively; similarly L_{PD} and L_{PP} – filterability of the volumetric flux resulting from the same forces.

However, to apply these laws to a finite-thickness membrane, it was necessary to change to integral forces expressed in terms of differentials of the same values Δx_1 and Δp. To do that, it was necessary to know how the local factors L_{DD}, L_{DP}, L_{PD} and L_{PP} depended on the pressure and molar concentration of one of the gases n_1. For this purpose the investigators applied to the Chapmen-Enskog's kinetic theory of ideal gas transport. According to this theory a little bit modified to the intermediate flow under consideration in-between the normal diffusion and Knudsen fluxes the binary gas in the porous membrane is approximated as a three-component system where one of the components is the membrane material itself as if distributed in the gas flow in the form of a more coarse suspended dust. The

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[1] To ascertain those conditions was the main task of the investigation mentioned.

said “dusted gas” model certainly comprised the Onsager’s symmetry conditions and provided explicit equations for diffusivity and filterability:

$$L_{DD} = (D_1/n_1\gamma_1 + D_2/n_2\gamma_2)/p(n_1\gamma_1 + n_2\gamma_2)\ , \qquad (15.2.3)$$

$$L_{PD} = L_{DP} = (D_1 - D_2)/p(n_1\gamma_1 + n_2\gamma_2)\ , \qquad (15.2.4)$$

$$L_{PP} = (n_1D_1 + n_2D_2)/p(n_1\gamma_1 + n_2\gamma_2) + B_o/\nu\ . \qquad (15.2.5)$$

Here $D_1 = (1/D_{1k} + 1/D_{12})$; $D_2 = (1/D_{2k} + 1/D_{12})$ – diffusion factors for argon and helium, respectively; $\gamma_1 = D_1/D_{1k}$; $\gamma_2 = D_2/D_{2k}$; D_{1k}, D_{2k} – Knudsen diffusion factor and inter-diffusion factors for argon and helium, respectively; B_o – membrane permeability; ν – dynamic viscosity of the system.

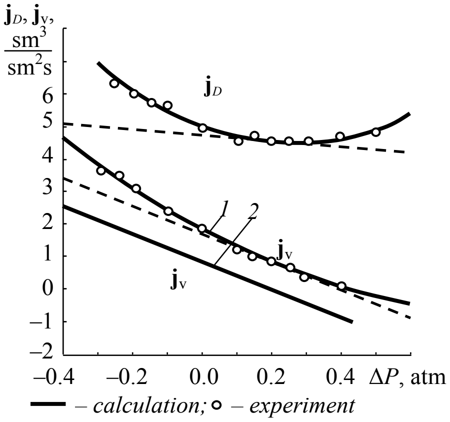
The said dependence of the factors L_{ij} in relationships (15.2.3)-(15.2.5) on the local pressure p and the molar concentrations n_1 and n_2 of the components on the membrane made the diffusion and filtration integral laws

$$\mathbf{j}_D = -L_{DD}^{\mathrm{cp}}\,\Delta x_1 - L_{DP}^{\mathrm{cp}}\,\Delta p\ , \qquad (15.2.6)$$

$$\mathbf{j}_V = -\mathrm{L}_{PD}^{\mathrm{cp}}\,\Delta x_1 - \mathrm{L}_{PP}^{\mathrm{cp}}\,\Delta p \qquad (15.2.7)$$

non-linear since the fields of pressures and concentrations in the membrane vary with the forces Δx_1 and Δp; the averaged factors L_{DD}^{av}, L_{DP}^{av}, L_{PD}^{av} and L_{PP}^{av} also appear to be an implicit function of these forces. Therefore the associated targets of this investigation were to check the applicability of the linear TIP and the ideal gas transport kinetic theory to this system. The calculated results of one series of such experiments at a constant mean gas pressure of $p = 1.96$ kg/cm^2 and a constant gas composition are plotted on Fig.15.2 as solid lines against the experimental values of the same parameters dotted (Mason, Wendt, Bresler, 1972).

As follows from the figure, the calculated from kinetic theory diffusion and volumetric flux densities $\mathbf{j}_D$ and $\mathbf{j}_V$ vs. pressure differential well agree with the experimental data and have a complex non-linear character complying with that experimentally found. At the same time both the experiment and the calculation reveal a violation of the Onsager’s symmetry conditions in the system under consideration, which aggravates with the system drifting from equilibrium. In fact, the tangent of $\mathbf{j}_D$ curve inclination defining the diffusivity L_{DP} changes not only its value, but also the sign, whereas the vertical segments in-between the curves $\Delta x_1 = 0{,}963$ and $\Delta x_1 = 0$ characterizing the symmetrical filterability L_{PD} change much less in value and does not change the sign at all. Only close to the point Δp = 0.2 atm, where volumetric flux becomes zero, while the $\mathbf{j}_D$ and $\mathbf{j}_V$ curves may be quite accurately approximated by the linear phenomenological laws, the Onsager's reciprocity relationships apply with relative accuracy. However, as experimenters stress, the space where the linear laws and the Onsager's reciprocity relationships are valid, becomes evanescent if equations (15.2.6)-(15.2.7) are integrated with the fluxes $\mathbf{j}_D$ and $\mathbf{j}_V$ related to the mean integral value of argon concentration (which ensued from the TIP requirement for invariance of dissipation function with change to new forces and flows). It is also significant that the tangents of $\mathbf{j}_D$ and $\mathbf{j}_V$ curves inclination are opposite on the major part of their length (at Δp > 0.2 atm), which evidences the anti-symmetrical character of the reciprocity relationships). This also contradicts the TIP stating the anti-symmetry conditions show in only the case when the forces $\boldsymbol{X}_D$ and $\mathbf{X}_V$ have different parity relative to time reversal (H. Cazimir, 1945). Meantime, in this case these forces do not change the sign when time "reverses", i.e. both of them refer to even time function. It is worth noticing that close to the stationary state ($\mathbf{j}_V$ = 0) the Onsager's reciprocity relationships apply despite the extremely possible drift of the system from material equilibrium ($\Delta x_1 \approx 1$), which evidences that the TIP requirement for a system to be immediately close to equilibrium is superfluous. Thus we encounter here the situation when practically none of the linear TIP known statements applies.



_______calculation;○ experiment

1 – Δx_{Ar} = 0.963; *2* – Δx_{Ar} = 0.

Fig.15.2. Superposition of Flows across Graphite Membrane

It becomes even more attractive to check the applicability of thermokinetics at these conditions. Note immediately that the independent diffusion and volumetric fluxes $\mathbf{j}_D$ and $\mathbf{j}_V$, as well as the volumetric flux motive force $\mathbf{X}_V = -\nabla p$, comply with the thermokinetic requirements. However, the diffusion flux motive force at S, V = const is the negative gradient of diffusion potential of any (e.g. the first) independent component

$\mathbf{X}_D = -\nabla\zeta_1$. Since the molar entropies s_{ko} and volumes υ_{ko} remain constant in this case, then according to (14.3.2)

$$\mathbf{X}_D = -\nabla\zeta_{k1} = -\nabla\mu_1, \tag{15.2.8}$$

so that it may be used a known representation of the ideal gas chemical potential μ_i in terms of its standard value μ_i^o and the partial pressure p_i

$$\mu_i = \mu_i^o + R_\mu T \ln p_i\,. \tag{15.2.9}$$

Applying the ideal gas equation $p_i = px_i = n_iR_\mu T$ (where x_i, n_i, R_μ – mole fraction of the i^{th} gas, its molar concentration and universal gas constant, respectively) the diffusion motive force may be expressed as $\mathbf{X}_D = -(R_\mu T/p_i)\nabla p_i$. Thus the forces $\mathbf{X}_D$ and $\mathbf{X}_V$ appear in this case to be interrelated so that the local diffusion and filtration laws should be written down in the matrix (Onsager's) form:

$$\mathbf{X}_D = R_{DD}\,\mathbf{j}_D + R_{DP}\,\mathbf{j}_V \tag{15.2.10}$$

$$\mathbf{X}_V = R_{PD}\,\mathbf{j}_D + R_{PP}\,\mathbf{j}_V \tag{15.2.11}$$

где R_{DD}, R_{DP}, R_{PD}, R_{PP} – phenomenological resistibility as inverse value to the phenomenological diffusivity and filterability L_{DD}, L_{DP} and L_{PD}, L_{PP}, respectively (S De Groot, P. Mazur, 1964).

To change to the integral form of these equations where the diffusion and filtration motive forces are expressed in terms of pressure differentials $\bar{\mathbf{X}}_D = -\Delta p_1$; $\bar{\mathbf{X}}_V = -\Delta p$), let us apply to the same phenomenological factors vs. pressure and concentration as in 15.2.3-15.2.5**.** Taking into consideration that $\bar{\mathbf{X}}_D = \int\mathbf{X}_D d\ell$; $\bar{\mathbf{X}}_V = \int\mathbf{X}_V d\ell$, where ℓ – membrane thickness, and given constancy of the $\mathbf{j}_D$ and $\mathbf{j}_V$ fluxes, gives that change to the integral form of laws (15.2.3) and (15.2.4) comes to calculation of the total resistibility to the said flows $\check{R}_{ij} = \int R_{ij} d\ell = \int L_{ij}^{\ 1} d\ell$. This leads to pseudo-linear integral laws of the following kind:

$$\bar{\mathbf{X}}_D = \check{R}_{DD}\,\mathbf{j}_D + \check{R}_{DP}\,\mathbf{j}_V \tag{15.2.12}$$

$$\bar{\mathbf{X}}_V = \check{R}_{PD}\,\mathbf{j}_D + \check{R}_{PP}\,\mathbf{j}_V \tag{15.2.13}$$

These laws differ from (15.2.6), (15.2.7) basically in the behavior of the diffusion motive force vs. the pressure differential across the membrane with the result that the non-linearity of the $\mathbf{j}_D$ curves becomes less distinct. It only remains to confirm the validity of generalized reciprocity relationships (4.5.3) for such processes. The computation results based on (15.2.3)-(15.2.5) for the same experimental conditions are described in Table 12-1 (V. Etkin, 1983).

As follows from the table, the generalized reciprocity relationships (columns 3 and 4) apply well enough for even the close-to-limit drift of the system from diffusion equilibrium. At the same time the computation results show the Onsager's reciprocity relationships go over into the Cazimir's anti-symmetry conditions thru the entire range of thermodynamic forces. This is caused by the fact that the concentration gradients across the membrane for argon and helium are counter-directed (i.e. are opposite in sign).

Table 12.1

Reciprocal Relations for Non-Linear Cross Diffusion of Helium and Argon

Motive forces, *atm*		Diff. reciprocal reltions, $cm^3/cm^2 \cdot s \cdot atm$		Onsager's symmetry conditions, $cm^3/cm^2 \cdot s \cdot atm$	
$\bar{\mathbf{X}}_D$	$\bar{\mathbf{X}}_V$	$\partial \mathbf{j}_D/\partial \bar{\mathbf{X}}_V$	$\partial \mathbf{j}_V/\partial \bar{\mathbf{X}}_D$	L_{DP}	L_{PD}
0	0	– 1.75	1.75	– 1.749	1.749
0	0.5	– 1.77	1.77	– 1. 765	1.915
0	0.9	– 1.83	1.82	– 1.837	2.12
0.5	0	– 1.91	1.905	– 1.875	1.85
0.5	0.5	– 1.70	1.76	– 1.786	1.97
0.5	0.9	– 1.21	1.25	– 1.81	2.15
– 0.5	0	– 1.75	1.77	– 1.835	1.745
– 0.5	0.5	– 2.87	2.96	– 1.85	2.08
– 0.5	0.9	– 4.51	4.55	– 1.89	2.21

In this case the equalization of concentration of one of the system components (argon) causes the "ascending diffusion" of the other component (helium), i.e. its motion toward its increased concentration. The two flows (argon and helium) become now interconnected ("related") so that an enhancement of one of them suppresses the other. This means that in the course of relaxation of one of the components useful work on the other one is being done. Since TIP does not consider the useful work processes, it could not predict this result. In this respect thermokinetics supplements the existing concepts regarding the origin of anti-symmetrical reciprocity relationships including in their number the cases of counteracting forces of the same parity. It follows also from Table 15.1 that the anti-symmetry conditions apply quite satisfactorily close to the stationary state associated with disappearance of the volumetric flux $\mathbf{j}_V$, though the system in whole stands in this case extremely far from material equilibrium (concentration differential close to unity). This confirms the deduction of thermokinetics that, to agree with the Onsager-Cazimir's symmetry conditions, it is enough that the cross terms in the Onsager's phenomenological laws be linear, which complies with partial (in this case, filtration) equilibrium. Thus we encounter in this example a situation when practically all statements of linear TIP do not come true.

15.3. Simplification of Transport Laws Based on Differential Reciprocal Relations

A significant advantage of the method for investigation of irreversible processes consists in the possibility to reduce the transport kinetic equations to the "diagonal" form containing a single (resultant) motive force. This allows dramatic reduction of the kinetic (empirical) factors these equations contain. This may be instantiated most clearly by the interrelation between anisotropic thermal conduction and electrical conduction of bodies in magnetic field.

Artificial anisotropy, viz. a distortion of current lines and heat stream in conductors placed in magnetic field, engenders a number of effects usually referred to the "thermo-galvano-magnetic" group and subdivided into "thermoelectric" (due to the interrelation between thermal and electric phenomena), "galvanomagnetic" (due to the interrelation between electric current and magnetic field) and "thermomagnetic" (due to the impact of magnetic field on heat flow), while depending on the magnetic field direction (lengthwise or across the conductor) – also into longitudinal and transversal. An empirical approach to the description of such phenomena is usually restricted to the 2D case (heat and charge streams lie in the x–y plane) and introduces the tensors of thermal conduction and electrical conduction thus providing a set of 6 interrelated equations (equal to the total number of the electric current and heat stream vectors' components) with 36 empirical factors (S. De Groot, 1956). Due to the isotropy of the system in the x–y plane only 12 factors of 36 remain independent.

These are the laws that served for L. Onsager as a prototype to his "matrix" phenomenological laws (4.4.1). According to these laws the electric charge and heat stream vectors' components are considered as independent flows, while the temperature gradient and electric potential vectors' components – as independent thermodynamic forces. The linear theory of irreversible processes (TIP) based on this assumption sets an additional interrelation between some of the abovementioned phenomena and reduces the number of the independent empirical factors to 9 due to the application of the Onsager-Cazimir's symmetry conditions (R. Haase, 1967).

Thermokinetics allows to go even further and to reduce the number of the said factors more than twice by imparting the thermodynamic form to the equations of anisotropic thermal conduction and electrical conduction. This becomes possible by applying the reciprocity relationships not *before*, but *after* the final (thermokinetic) form of anisotropic thermal and electrical conductivities has been determined.

According to thermokinetics the artificial anisotropy of electrical conduction may be allowed for by proceeding from the traditional definition of work as the product of a force and the distance the object covers under this force applied. According to (2.4.7), providing the force direction does not coincide with the travel direction as it takes place in anisotropic bodies, the dissipation function (dissipation process power) should be represented as:

$$N^d = \Sigma_i \,|\mathbf{X}_i|\cdot|\mathbf{j}_i|\cos\gamma_i\,, \qquad (15.3.1)$$

where γ – angle between the vectors $\mathbf{X}_i$ and $\mathbf{j}_i$.

From this it follows that the thermodynamic form of Ohm's and Fourier laws for bodies with artificial anisotropy requires the angle γ_e between the anisotropic electrical conduction motive force $\mathbf{X}_e{}^a$ and the current vector $\mathbf{j}_\mathrm{e}$ to be allowed for, as well as the angle γ_q between the anisotropic thermal conduction motive force $\mathbf{X}_\mathrm{q}{}^\mathrm{a}$ and the entropy flow $\mathbf{j}_\mathrm{s}$:

$$\mathbf{j}_e = \sigma_e \mathbf{X}_e{}^a \cos\gamma_e = L_e (\mathbf{X}_e{}^a)\, \mathbf{X}_e{}^a \,, \qquad (15.3.2)$$

$$\mathbf{j}_s = (\lambda/T)\mathbf{X}_q{}^a \cos\gamma_q = L_q (\mathbf{X}_q{}^a)\mathbf{X}_q{}^a \,, \qquad (15.3.3)$$

where λ, σ_e – thermal conductivity and electric conductivity, respectively, in the absence of magnetic field; $L_q(\mathbf{X}_q{}^a) = \lambda\cos\gamma_q /T$; $L_e(\mathbf{X}_e{}^a) = \sigma_e\cos\gamma_e$ – phenomenological coefficients as functions of the thermodynamic forces $\mathbf{X}_s{}^a$ and $\mathbf{X}_e{}^a$ thru the angles γ_q и γ_e.

Before obtaining an extended expression for these laws, let us find their thermodynamic form in the absence of anisotropy. We will consider electrical conduction in metals as a particular case of the diffusion in a multi-component system where free electrons are the only movable component (Groot, Mazur, 1964). The chemical potential μ_k for a multi-component system with components carrying the electrical charge per mass unit ϑ_{ek} is known to give place to the electrochemical potential $\mu_k{}^* = \mu_k + \vartheta_{ek}\varphi$, where φ – electrical potential of a particular zone in the system. Therefore assuming the "electron gas" to be, as usual, one of the components of the system "free electrons + ions" and the uniqueness conditions for the diffusion of free electrons to be the same as in the diffusion of the k^{th} component, gives the additional term $\vartheta_{ek}\nabla\varphi$ appearing in the equation for the thermodynamic force $X_k = -\nabla\zeta_k$ of this process:

$$X_k = -\, [\Sigma_k\mu_{k\ell}\nabla c_\ell + (s_k - s_{ko})\nabla T - (\upsilon_k - \upsilon_{ko})\nabla p + \vartheta_{ek}\nabla\varphi]. \qquad (15.3.4)$$

Since mechanical equilibrium ($\nabla p = 0$) takes place in the system under consideration and the gradient of ion concentration (second component) is absent, i.e. $\nabla c_\ell = 0$, the expression for the diffusion flux of the k^{th} component in electrolytes becomes:

$$\mathbf{j}_k = -\, L_{kk}\, [\vartheta_{ek}\nabla\varphi + (s_k - s_{ko})\nabla T]. \qquad (15.3.5)$$

To endue this equation with the form of Ohm's generalized law, it is necessary to change to the electrical charge flux with the k^{th} component $\mathbf{j}_e = \vartheta_{ek}\mathbf{j}_k$ and to simultaneously introduce the related force $\mathbf{X}_e$ proceeding from the product $\mathbf{j}_k{\cdot}\mathbf{X}_k$ to be maintained (dissipation function invariance). This condition is associated with the force $\mathbf{X}_e = \mathbf{X}_k/\vartheta_{ek}$ so that Ohm's generalized law becomes:

$$\mathbf{j}_e = \sigma_e \mathbf{X}_e = \sigma_e [\mathbf{E} + \mathbf{X}_{eq}] , \qquad (15.3.6)$$

where $\mathbf{E} = -\nabla\varphi$ – electric field; $\mathbf{X}_{eq} = - s_e^* \nabla T$ – thermodynamic representation of the so-called "thermomotive force"; $s_e^* = (s_e - s_{eo})$ – specific (per charge unit) electron transport entropy (Haase, 1967); $\sigma_e = L_{kk}\vartheta_{ek}^2$.

Thus there is an additional force of $\mathbf{X}_{eq}$ appearing along with EMF in conductors with inhomogeneous temperature field and responsible for homogeneous thermoelectric effects (Etkin, 1991). In magnetic field it is supplemented with the Lorenz force $\mathbf{F}_L = \mathbf{v}_e \times \mathbf{B} = \upsilon_e \mathbf{j}_e \times \mathbf{B}$ (where $\mathbf{v}_e$, $\mathbf{B}$ – electron transport velocity and magnetic flux density, respectively; υ_e, $\mathbf{j}_e$ – specific volume of "electron gas" and current density, respectively). This force is a normal to the current direction and, therefore, does not do any (including dissipation) work. However, this is the force responsible for the artificial anisotropy of the initially isotropic heat and charge conductors since it changes the direction of current and heat stream and thus – the projection of the anisotropic electrical conduction resultant force $\mathbf{X}_e^a = \mathbf{E} + \mathbf{X}_{eq} + \mathbf{F}_L$ on the electron transport direction. Given this force, Ohm's law acquires the following extended thermodynamic form:

$$\mathbf{j}_e = - \sigma_e \cos\gamma_e [\nabla\varphi + s_e^* \nabla T + \upsilon_e \mathbf{j}_e \times \mathbf{B}] , \qquad (15.3.7)$$

where

$$\cos \gamma_e = |\mathbf{X}_e| / |\mathbf{X}_e^a| = 1 - |F_L| / |X_e^a| . \qquad (15.3.8)$$

The dependence of cos γ_e on the current density j_e makes the anisotropic electrical conduction law (see 15.3.7), strictly speaking, non-linear.

To determine the thermodynamic form of Fourier law for the case of anisotropic thermal conduction, let us use the generalized reciprocity relationships (see 4.5.3) which have the following form for the case under consideration:

$$(\partial \mathbf{j}_e / \partial \mathbf{X}_q^a) = (\partial \mathbf{j}_s / \partial \mathbf{X}_e^a) . \qquad (15.3.9)$$

Given (15.3.8) and the independence of $\nabla\varphi$ on $\mathbf{X}_q^a$, one can find at $\mathbf{X}_e^a$ being constant:

$$(\partial \mathbf{j}_e / \partial \mathbf{X}_q^a) = \mathbf{X}_e^a (\partial L_e / \partial \mathbf{X}_q^a) = \sigma_e \mathbf{X}_e^a (\partial \cos \gamma_e / \partial \mathbf{X}_q^a) = - \sigma_e s_e^* . \qquad (15.3.10)$$

Then according to (15.3.9) with the components $\mathbf{F}_L$ and $\mathbf{X}_{eq}$ of the force $\mathbf{X}_e^a$ being constant:

$$(\partial \mathbf{j}_s / \partial \mathbf{X}_e^a) = (\partial \mathbf{j}_s / \partial \mathbf{E}) = -\sigma_e s_e^* . \qquad (15.3.11)$$

This means that an additional term, viz. $-\sigma_e s_e^* \mathbf{E}$, appears in the thermodynamic form of Fourier law generalized for the anisotropic thermal conduction case:

$$\mathbf{j}_s = -(\lambda/\mathrm{T})\nabla T - \sigma_e s_e^* \mathbf{E} . \qquad (15.3.12)$$

The found diagonal form for the equations of anisotropic thermal and electrical conductions allows obtaining all superposition effects inherent for such systems from the equilibrium conditions, i.e. by the same method as described in the previous chapter.

15.4. Further Reduction of the Number of Kinetic Factors in Transport Equations

Let us apply the found equations of anisotropic thermal and electrical conductions to determine the analytical expressions for the abovementioned superposition effects. Let us start off with the magneto-resistive effects consisting in resistance variation of the conductors in magnetic field and used for the magnetic field measurement (in magnetometers).

From the positions of thermokinetics these effects are explained by the deviation of the current direction from the electric field direction **E**. If, for the sake of demonstrativeness (see Fig.15.3), the field direction **E** coincides with the axis x, then at $\nabla T = 0$ the current direction will make the angle γ_e with this axis, while the current component along this axis, $j_{ex}(\mathbf{B})$, in the transverse magnetic field will vary by a factor of $\cos\gamma_e$ against its value without the field, which, according to the definition method of the electric conductivity $\sigma_e = \mathbf{j}_e/\mathbf{E}$, will lead to reducing this conductivity in the transverse magnetic field down to σ_e'':

$$\sigma_e'' = j_{ex} / \nabla_x \varphi = \sigma_e \cos\gamma_e , \qquad (15.4.1)$$

where $\nabla_x \varphi$ – projection of the vector $\nabla\varphi$ on the axis x.

As next step, let us consider thermoelectric effects in the presence of magnetic field. Let the conductor plane and the current therein (see Fig.15.3) are oriented in the magnetic field direction, i.e. along the axis z ($\mathbf{j}_e = j_{ez}$). Then the angle between the vectors $\mathbf{j}_\mathrm{e}$ and $\mathbf{B}$ is equal to zero, so Ohm's law becomes:

$$j_{\mathrm{e}z} = -\,\sigma_\mathrm{e} \cos\gamma_\mathrm{e}\, [\nabla_z \varphi + s_\mathrm{e}{}^{*}\nabla_z T], \tag{15.4.2}$$

where $\nabla_\mathrm{z}\, \varphi$, $\nabla_\mathrm{z}\, T$ – projections of the vectors $\nabla\varphi$ and ∇T on the current direction.

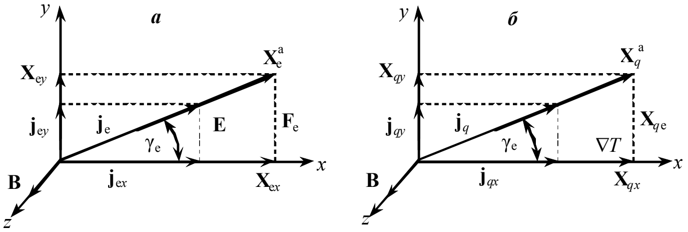


Fig.15.3. Thermal Conductance & Electrical Conductance Anisotropy

As follows from this expression, the electric current is a result of the joint action of the thermoelectric force $s_\mathrm{e}{}^{*}\nabla_\mathrm{z}T$ and the electric field $\nabla_\mathrm{z}\varphi$. And otherwise, the current flow in the conductor generates a heterogeneous temperature field with the conductor surface releasing (or absorbing) the Thomson heat $q_\mathrm{T}{}^{*} = Ts_\mathrm{e}{}^{*}$ which is similar to the transport heat $q_k{}^{*}$ of the k^{th} component. That phenomenon was first predicted by Thomson in his theory of thermoelectricity (1864) and has been called Thomson effect since that time. From the expression for the Thomson specific heat $q_\mathrm{T}{}^{*}$ it follows that the Thomson effect value is proportional to the current density $\mathbf{j}_\mathrm{e}$, while for the conductor as a whole – to the displacement current therein, which has been experimentally confirmed (R. Haase, 1967). It is worth mentioning the stationary state supported by the thermal conductance process and featuring the current disappearing ($j_{ez} = 0$) due to the thermodynamic force $\mathbf{X}_e$ components mutually balanced out in (15.3.7). This phenomenon is called the Thomson stationary effect and estimated as the electric potential gradient related to the temperature gradient in a conductor de-energized ($j_{ez} = 0$):

$$\alpha_T' = (\nabla_z\varphi/\nabla_z T)_{\mathrm{st}} = s_{\mathrm{e}}^*, \qquad (15.4.3)$$

where α_T' – thermoelectric motive force coefficient [1].

The similar effect appears in the transverse magnetic field as well when the current is directed along the axis x. In this case in Ohm's law (15.3.7) $\mathbf{j}_e = j_{ex}; \nabla\varphi = \nabla_x\varphi; \nabla T = \nabla_x T$. For stationary conditions ($j_{ex} = 0$) from (15.3.7) the expression for the Thomson cross effect follows as:

$$\alpha_T'' = -(\nabla_x \varphi/\nabla_x T)_{\mathrm{st}} = s_{\mathrm{e}}^*. \qquad (15.4.4)$$

Now let us consider the thermomagnetic effects. One of them – Righi-Leduc effect – means a temperature gradient arising in the direction normal to the heat flow $\mathbf{j}_q$ and the field $\mathbf{B}$ in the absence of current ($\mathbf{j}_e = 0$). This effect is as well caused by the abovementioned thermal conductance anisotropy in magnetic field. If, for the sake of convenience, the heat stream direction coincides with the axis x and given the vector ∇T makes the angle γ_q with this axis (see Fig. 15.4), the components $\nabla_x T$ and $\nabla_y T$ will be evidently interrelated as:

$$\alpha_{\mathrm{RL}}\, \mathbf{B} = (\nabla_y T/\nabla_x T) = \mathrm{tg}\,\gamma_q \; (\mathbf{j}_{\mathrm{e}} = 0), \qquad (15.4.5)$$

where α_{RL} – Righi-Leduc coefficient.

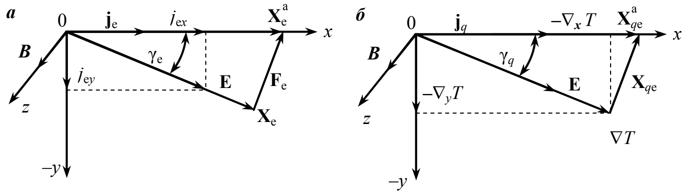


Fig.15.4. Definition of Thermo-Galvano-Magnetic Effects

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[1] The left-hand side of the expression for an adequate effect will hereafter everywhere contain the coefficient corresponding to the empirical description of this particular phenomenon in the monograph by R. Haase, 1967.

That effect was discovered almost simultaneously by A. Righi and S. Leduc (1887). It is usually represented as the product of some constant α_{RL} and the magnetic intensity **B** thus stressing the proportionality of this effect to the field **B**. Note – this fact directly ensues from (12.4.4) thereby confirming the deductions of thermokinetics.

Another thermomagnetic effect consists in the emergence of a weak electrical field of $\nabla_y\varphi$ in a de-energized conductor containing a temperature gradient of ∇T caused by the heat flow $\mathbf{j}_q$ in the direction normal to the field intensity **B**. That effect was discovered by *W*. Nernst and A. Ettinshausen (1886) and has borne their names since that time. It can be more conveniently described with the vector ∇T oriented along the axis x (see Fig.15.4). Then $\nabla T = \nabla_x T$ and, given the evident relation $\nabla_y\varphi/\nabla_x\varphi = \mathrm{tg}\gamma_e$ (Fig.15.4), the desired relationship can be represented as:

$$A_{EN}\mathbf{B} = -(\nabla_y\varphi/\nabla_x T) = -(\nabla_x\varphi/\nabla_x T)(\nabla_y\varphi/\nabla_x\varphi) = s_e^* \mathrm{tg}\,\gamma_e\,, \qquad (15.4.6)$$

where α_{EN} – Ettinshausen–Nernst constant. The proportionality of this effect to the field **B** is also experimentally confirmed.

Let us now consider the group of galvanomagnetic effects in more detail. Hall effect discovered in 1879 is the best known of them. It consists in the emergence of the electrical field **E** in the direction normal to the electrical current $\mathbf{j}_e$ and the magnetic field **B**. To derive the Hall effect analytically, let us align the axis x with the current density $\mathbf{j}_e$ vector (Fig. 15.4). Then $j_{ey} = 0$; $\mathbf{j}_e = j_{ex}$, while the force $\mathbf{X}_e$ will make an angle of γ_e with the axis x so that its component along the axis y will become equal to $\nabla_y \varphi = \nabla_x \varphi\ \mathrm{tg}\gamma_e$. Taking into account that in a conductor thermally homogeneous $\mathbf{j}_e = -\sigma_e''\nabla_x\varphi$ gives:

$$\alpha_H\mathbf{B} = -(\nabla_y \varphi / j_{ex})_{cT} = \mathrm{tg}\,\gamma_e/\sigma_e''\ (j_{ey} = 0\,), \qquad (15.4.7)$$

where α_H – Hall constant.

From (15.4.7) it directly ensues that Hall constant is nothing else but the specific volume per electrical charge unit (positive or negative). Therefore the Hall effect sign depends on the charge carrier sign, while the Hall effect value – on the charge carrier concentration. These facts make Hall effect one of the most efficient methods for investigating the charge energy spectrum in metals and semiconductors. It is also used for measurement of magnetic intensity, for current multiplication in analog computers and in some kinds of MHD-current generators.

Another effect also discovered by Nernst in 1887 and bearing his name consists in the emergence of a temperature gradient of $\nabla_x T$ in the direction of the current $\mathbf{j}_e = j_{ex}$ with the transverse magnetic field available when the heat flow $\mathbf{j}_q$ is absent. This effect differs from the Thomson thermoelectric effect because arises in a conductor that initially is thermally homogeneous. This effect results from setting the stationary state when the heat stream ceases. Then substituting the product $\sigma_e \mathbf{E}$ for j_{ex} in Fourier's generalized law (15.4.5) gives that at this state $j_{sx} = -(\lambda''/T)\nabla_x T + s^*_{\mathrm{e}} j_{\mathrm{e}x} = 0$. From this it directly follows that

$$\alpha_{\mathrm{N}} = (\nabla_x T / j_{\mathrm{e}x})_{\text{ст}} = T s^*_{\mathrm{e}} / \lambda'' \; (j_{\mathrm{e}y} = 0\,), \tag{15.4.8}$$

где α_{N} – Nernst constant; λ'' – thermal conductivity in the transverse magnetic field.

The effect of a temperature gradient of $\nabla_z T$ emerging in the magnetic field direction is similar to the Nernst effect providing the current flows in the same direction $j_e = j_{ez}$, while the system in this condition is thermally homogeneous. This phenomenon does not have a special name – R. Haase proposed to call it Kelvin effect. Expressing, similar to the above, Fourier's law for the heat flow along the axis z gives $j_{sz} = -(\lambda/T)\nabla_z T + s^*_{\mathrm{e}} j_{\mathrm{e}z}$, so that with the stationary state setting in:

$$\alpha_{\mathrm{K}} = (\nabla_z T / j_{\mathrm{e}z})_{\text{ст}} = T s^*_{\mathrm{e}} / \lambda \quad (j_{\mathrm{e}x} = 0)\,, \tag{15.4.9}$$

where α_{K} is a value R. Haase proposed to call Kelvin constant.

Ultimately, there is one more effect among the galvanomagnetic effects, which was also discovered by Ettinshausen in the mentioned 1887 and consists in the emergence of a temperature gradient of $\nabla_y T$ in the direction normal to the current $\mathbf{j}_e = j_{ex}$ and the field $\mathbf{B}$. It is also caused by the different directions of the vectors $\mathbf{X}_e$ and ∇T. If, by way of explanation, the axis x coincides with the current $\mathbf{j}_{\mathrm{e}}$ direction, then the components $\nabla_{\mathrm{y}} T$ and $\nabla_x T$ will be interrelated thru $\mathrm{tg}\gamma_q$. Then substituting the expression $\nabla_y T\, \mathrm{tg}\gamma_q$ into (15.4.9) gives instead of $\nabla_x T$:

$$\alpha_{\mathrm{E}} \mathbf{B} = (\nabla_y T / j_{\mathrm{e}x})_{\mathrm{st}} = T s^*_{\mathrm{e}} \mathrm{tg}\,\gamma_q / \lambda'' \; (j_{\mathrm{e}y} = 0), \tag{15.4.10}$$

где α_E – Ettinshausen constant.

Thus the entire spectrum of the thermoresistive, thermoelectric, thermomagnetic and galvanomagnetic effects in the longitudinal and transverse magnetic fields may be expressed using only 4 phenomenological coefficients (λ, λ'', σ_e,σ_e''). This substantially facilitates their theoretical analysis and experimental investigation.

15.5. Setting Additional Constraints between Superposition Effects

The above-found thermo-galvano-magnetic effects allow setting a number of relationships between them earlier obtained in TIP based on the Onsager-Cazimir's reciprocity relationships. This is first of all the Bridgeman's relationship (1929) connecting the Ettinshausen-Nernst effect with the Ettinshausen effect:

$$T\alpha_{EN} = \lambda''\alpha_E \ . \qquad (15.5.1)$$

This relationship can be also obtained from thermokinetics by comparing expressions (15.4.6) and (15.4.10). Another relationship connects the Nernst effect with the Thomson effect in the transverse magnetic field:

$$\alpha_N = T\, \alpha_T''/\lambda''. \qquad (15.5.2)$$

This relationship generalizes the thermoelectric effects to the systems in the transverse magnetic fields. It can be also obtained by directly comparing expressions (15.4.9) and (15.4.8). A similar relationship takes place in the longitudinal magnetic field as well:

$$\alpha_K = T\alpha_T'/\lambda. \qquad (15.5.3)$$

This expression extends the Thomson relationships obtained for thermocouples to particular current-carrying conductors. It can be also obtained by comparing expressions (15.4.8) and (15.4.14).

At the same time thermokinetics allows obtaining 5 additional relationships between the thermo-galvano-magnetic effects. One of such relationships directly ensues from comparing the thermo-EMF coefficients in the longitudinal and transverse fields (see 15.4.8 and 15.4.9), which evidences the identity of the Thomson longitudinal and transverse effects:

$$\alpha_T' = \alpha_T'' = s_e^* \qquad (15.5.4)$$

This provision, as well as the representation of the Thomson effect in terms of the transport entropy, did not ensue from TIP. It means that the thermo-EMF value does not depend on magnetic field – only the thermo-EMF direction varies and to the same extent as the direction of the heat stream creating this EMF. From this a physically significant conclusion follows about the coincidence of the angles γ_q and γ_e, i.e. about a *unified mechanism of the magnetic field impact on both the heat and electrical charge flows*, which allows definition of the angle $\gamma = \gamma_e = \gamma_q$ by measuring the magnetoresistive effect (see 15.4.6):

Another relationship, due to $\gamma = \gamma_e = \gamma_q$, connects the Ettinshausen effect (15.4.10) with the Nernst effect (15.4.8):

$$\alpha_N \, \mathrm{tg}\gamma = \alpha_E B \ . \qquad (15.5.5)$$

One more relationship connecting the Righi-Leduc and Hall effects can be obtained by comparing expressions (15.4.5) and (15.4.7) given the equality $\gamma_e = \gamma_q$:

$$\alpha_{RL} = \sigma_e'' \alpha_H \ . \qquad (15.5.6)$$

That relationship was earlier set within the electron theory of metals and many times experimentally confirmed.

The relationship between the Righi-Leduc (15.4.5) Ettinshausen-Nernst (15.4.6) effects can be found in the same way:

$$\alpha_{EN} = s_e^* \alpha_{RL} \ . \qquad (15.5.7)$$

Considering relationships (15.5.6) (15.5.7) jointly gives Wiedemann-Franz law stating constancy of the metal thermal conductance/electric conductance ratio:

$$\Lambda = \lambda''/T\sigma_e'' = \alpha_H \alpha_{EN} / \alpha_{RL} \alpha_E \ , \qquad (15.5.8)$$

where Λ is the so-called Lorenz constant. Thus Wiedemann-Franz law, as well as relationship (15.5.6), take a character of the deductions of thermokinetics. This shows, in particular, in the fact that all the above thermomechanical, thermochemical, thermoelectric and thermo-galvano-magnetic effects appear to be expressed in terms of the exclusively thermodynamic variables. This fact, as well as the possibility to set additional relationships between the superposition effects, results from the interrelation between the diagonal and non-diagonal phenomenological coefficients in the Onsager's phenomenological laws having been taken into account. To reveal the nature of such a relation, let us apply again to the thermokinetic form of transport equations (2.6.11) and (14.3.1) deriving them for a particular case of transporting any k^{th} substance in the form:

$$\mathbf{J}_k = K_k\, \Sigma_i\, \mathbf{F}_{ki} = L_k \mathbf{X}_k\,, \tag{15.5.9}$$

where $\mathbf{F}_{kj} = \alpha_{kj} \nabla \psi_j$ – components of the resultant force $\mathbf{X}_k = -\nabla \psi_k$; $\alpha_{kj} \equiv \mu_{k\ell}$, s_k^*, θ_{ek}, υ_k, etc. – thermodynamic values associated with the generalized potential gradients $\nabla \psi_j \equiv \nabla c_\ell, \nabla T, \nabla \varphi, \nabla p$, etc.

To return to the matrix form of the phenomenological laws adopted in TIP, let us introduce new phenomenological coefficients $L_{kj} = L_k \alpha_{kj}$. Тогда

$$\mathbf{j}_k = \Sigma_j L_{kj} \mathbf{X}_j\,. \tag{15.5.10}$$

It can be easily noticed that in such (onsager's) form of phenomenological laws the non-diagonal coefficients L_{kj} $(k \neq j)$ are connected with the diagonal coefficients $L_{kk} = L_k \alpha_{kk}$ thru a simple relationship:

$$L_{kk} / \alpha_{kk} = L_{kj} / \alpha_{kj} = L_k\,. \tag{15.5.11}$$

The relationship of such a kind may be instantiated by the above-found relation between the diagonal and non-diagonal diffusivities. Thus the definition of the thermodynamic form of phenomenological laws (14.3.1) is equivalent to imposing $(n - 1)$ additional constraints between the diagonal L_{kk} and the non-diagonal L_{kj} phenomenological coefficients by representing their ratio in terms of relations of the corresponding thermodynamic parameters:

$$L_{kj}/L_{kk} = \mathbf{X}_{kj}/\mathbf{X}_j = \alpha_{kk}/\alpha_{kj}\ . \qquad (15.5.12)$$

This becomes possible because the kinetic factors conditioning these coefficients (permeability of membranes, mobility of components, etc.) equally enter in both L_{kk} and L_{kj} with no impact on their ratio. The number of such constraints in each of the equations of the (12.5.11) type is evidently equal to $(n–1)$, which gives, with n of such equations, $n(n–1)$ constraints of the (12.5.12) type and allows reducing the number of the phenomenological coefficients from n^2 in empirical description down to n, whereas TIP reduces the number of such coefficients to only $n(n+1)/2$. In particular, to describe the diffusion, thermal diffusion and pressure diffusion of the k^{th} substance, one kinetic factor (along with the thermodynamic factors) appears to be sufficient, while, to describe anisotropic thermal conductance and electric conductance in the longitudinal and transverse magnetic field, per one thermal conductivity and electric conductivity $(\lambda , \lambda'', \sigma_e, \sigma_e'')$ are sufficient. In this respect the thermokinetic approach may be considered as a final stage of the transition from a purely phenomenological (pre-thermodynamic) investigation of a phenomenon to a thermodynamic-phenomenological investigation and further – to a purely thermodynamic one.

Chapter 16

SPECIFICITY OF TRANSFER PROCESSES IN BIO-SYSTEMS

One of the most characteristic features of bio-systems consists in the structuring processes running therein with a higher level of their heterogeneity (non-uniformity) and enhanced interrelations between them. In the late 19th century H. Driesch, a prominent German embryologist, based on a comprehensive experimental data proved that not only and not so much embryo cells as themselves would define bio-structure formation processes, but rather their position in the germinating embryo considered as a single whole, whence it followed that the properties of a whole bio-system would not mean the sum of its constituents' properties, but should be considered as a single spatially heterogeneous system. This concept underlies the principles of theoretical biology E. Bauer has formulated. His first principle reads as follows, “All living systems are never being in equilibrium but permanently doing work at the expense of their free energy against equilibrium required by the laws of physics and chemistry under existing environmental conditions”.

16.1. Vector Character of Biochemical Reactions

The useful (ordered) work can be provided in according to expression (2.3.7) by solely the forces of vector character $\mathbf{F}_i$ or $\mathbf{X}_i$ enabling the transport of the object they are applied to at the distance $d\mathbf{R}_i$. The validity of this statement is confirmed by all available operation experience of various power units. The chemical sources of electric energy, where for this purpose the spatial separation of reagents and, respectively, electrodes is provided, are not either exclusion. In the absence of that stated chemical reactions inevitably acquire the thermodynamically irreversible character, while their chemical affinity is realized in the form of the released dissipation heat equivalent to work. The affinity of homogeneous chemical reactions relates therefore in TIP entirely to the dissipation heat wells (see 4.1.3). Nevertheless, the EMF of galvanic or fuel cells found by the chemical affinity value corresponded to its experimental values. That had not resulted in any conflicts until a contradiction with Curie law was revealed. This law, as it has already been noted in Chapter 4, ensues from the condition of conservation of constraints at the transformation of coordinates and excludes the possibility of association (interrelation) of the phenomena having different tensor order and kind. In the context of transfer phenomena this means that the generalized rate of whatever process (flow $\mathbf{J}_\mathrm{i}$) in the equations of (4.4.1) type may depend on only the thermodynamic forces $\mathbf{X}_\mathrm{j}$ of the same (or even) tensor order (S. De Groot, P. Mazur, 1967). In the case under consideration this means that the homogeneous chemical reactions can not interact with the transfer processes bearing vector character. Due to the absence in classic thermodynamics the notion of internal work this fact has for a long time been passed unheeded and has up to date impeded the comprehension of impossibility to measure the useful work W^e in terms of the Gibbs’ energy decrease.

This conflict may be settled with the help of thermokinetics stating the difference in tensor order between the motive forces and the coordinates of ordered and disordered works, as well as the vector character of transfer processes and the chemical energy conversion for substances in biological membranes. To show this, let us consider an arbitrary r^{ht} chemical reaction with the k^{th} substances running in an open system of a type of flow reactor, fuel cell, plasma membrane, etc. In this case the flow $\mathbf{J}_k$ of the k^{th} substance is related with the total flow of reacting mixture $\mathbf{J}_c$ thru the evident relationship $\mathbf{J}_k = \mathbf{J}_c c_k$, where $c_k = N_k/N$ – current (local) value of molar concentration of the k^{th} substance in a particular cross section of the flow reactor. Expressing the c_k value by a known way in terms of its value c_{ko} at the flow reactor inlet, the degree of completeness ξ_r of the r^{th} reaction and the stoichiometric coefficients ν_{kr} of the k^{th} substances in this reaction (R. Haase, 1967; I. Gyarmati, 1974) gives:

$$c_k = c_{ko} + \Sigma_r \nu_{kr} \xi_r . \tag{16.1.1}$$

According to this expression the variation in the concentration c_k of the k^{th} substance in an open system occurs both due to the diffusion of the substances not participating in the chemical reactions (i.e. by equilibrium mass transfer) across the system borders and due to the internal chemical conversions. Now let the motive force $\mathbf{X_c}$ enabling the transfer of reacting mixture composed of the k^{th} substances be expressed in terms of the negative gradient of mixture chemical potential $\mathbf{X}_c = -\nabla\mu_c = -\Sigma_k\nabla(\mu_k c_k)$. Substituting this force into expression (16.1.1) reveals it as the algebraic sum of motive forces enabling the processes of two kinds:

$$\mathbf{X}_c = -\Sigma_k\nabla(\mu_k c_{ko}) - \Sigma_r \nabla\psi_r = \Sigma_k \mathbf{X}_k + \Sigma_r \mathbf{X}_r . \tag{16.1.2}$$

Here $\psi_r = \mathrm{A}_r(1-\xi_r)$ – local potential of the r^{th} flow reaction; $\mathbf{X}_k = -\nabla(\mu_k c_{ko})$ – motive force enabling the transfer of the k^{th} substances not participating in the chemical reaction (diffusion); $\mathbf{X}_r = -\nabla\psi_r$ – motive force of the r^{th} flow reaction. Both forces have certainly the same tensor order, which evidences the vector character of such reactions.

From expression (16.1.2) it also follows that each summand of its first sum, including the term $\Sigma_r \mathrm{A}_r d\xi_r$ describing the r^{th} scalar chemical reactions in homogeneous media, receives the matching additional summand of the second sum $\Sigma_r \mathbf{X}_r \cdot \mathbf{J}_r$ having vector character and describing in this case the chemical reactions running in the flow (in galvanic and fuel cells, plasma membranes, Van't Hoff's box, etc.). The meaning of the motive forces $\mathbf{X}_r$ of such reactions and their generalized rates (flows of reagents $\mathbf{J}_\mathrm{r}$) is unambiguously defined by the general expression $\mathbf{X}_i \equiv -\nabla\psi_i$ и $\mathbf{J}_i = \Theta_i\mathbf{v}_i$. In this case the motive force of the r^{th} chemical reaction means, as also in other cases, the negative gradient of the local potential $\psi_r = A_r(1 - \xi_r)$ pertaining to this reaction in a particular section of the flow reactor or plasma membrane, while the generalized rate of the process means the flow $\mathbf{J}_r$ of the reagents participating in this reaction:

$$\mathbf{J}_r = -L_r\,\Sigma_r\nabla\psi_r, \tag{16.1.3}$$

Thus under the conditions of spatial separation of reagents chemical reactions take the directional (vector) character, which causes their interaction with transfer processes in the full compliance with Curie law. The validity of this law for chemical reactions can be easily confirmed with the reagents preliminarily mixed before fed to the electrodes of a fuel or galvanic cell: their EMF will then drop to zero, while the reaction becomes thermodynamically irreversible.

16.2. Interrelation between Active and Passive Transport Processes in Biosystems

One of the major targets of modern biophysics consists in stating laws describing principles and processes of functioning living organisms. Thermokinetics is most applicable to these targets. Firstly, it considers each cell of a bio-system as a spatially heterogeneous system being the same full-value micro-organism as the whole organs and organisms these cells form. Secondly, unlike non-equilibrium thermodynamics, thermokinetics is not limited to studying dissipation processes, but considers, along with them, also the processes of useful energy conversion inseparably associated with the vital activity of bio-organisms (E. Bauer, 1930). Thirdly, it is not limited to the stationary non-equilibrium states, as TIP is, and allows investigating the cyclic state variations characteristic for bio-organisms at all stages of their evolution. Fourthly, it is applicable to also the states which are, like bio-systems, rather far from equilibrium. Therefore the methods of thermokinetics are most adequate to the circle of the problems biophysics and bioenergetics solve.

One of such problem consists in determining the motive forces and generalized rates of biological processes. Specific role among them play the reactions of adenosine triphosphate (ATP) synthesis from the molecules of carbohydrates and fats nutrients contain and the reactions of the ATP subsequent decomposition. The biochemical reactions of ATP synthesis proceed with useful work done and both the cell and the system in whole withdrawing from the state of equilibrium. This is achieved due to the active transport of substances in biological membranes (i.e. due to their transfer in the direction of increasing concentration). The differentials of chemical potentials thus generated enable then the passive transport of the reagents to the reaction zone. The combination of these processes provides the cyclic process of ATP synthesis and subsequent decomposition with the associated energy consumption and release.

The determination of such forces and rates is currently provided based on expression (4.1.4) for the entropy generation rate. Meantime the application of TIP to analysis of reversible processes is a method involving certainly unfit means. The useful work bio-systems do in the course of their vital activity relates, as per classic thermodynamics, to adiabatic processes which in principle can not cause entropy variations. Therefore the entropy generation can not assure correct value of the motive forces for biological processes since their reversible component does not impact the entropy. E.g. the EMF of a reversible galvanic element derived from (4.1.4) will appear to be close to zero, the same for the entropy generation itself in this particular case.

Furthermore, expression (4.1.4) can not be basic for even the definition of the sign pertaining to these forces. In fact, in the active transport processes the k^{th} substances are transferred toward their increased concentration, i.e. the $\mathbf{J}_k$ flows are directed against the motive forces $\mathbf{X}_k$. In this case the product $\mathbf{X}_k \cdot \mathbf{J}_k$ is always negative. Meantime, all the summands of (4.1.4) are always non-negative as characterizing the share of any of the independent irreversible processes in the entropy production. It is easy to ascertain this if noticing that the sign of the derivative $X_i = (\partial S/\partial \alpha_i)$ always coincides with the sign of the force since the entropy production is always non-negative. In these cases the authors of many study guides interpret the situation $\mathbf{X}_k \cdot \mathbf{J}_k < 0$ as the “nega-entropy production”, “negentropy consumption”, etc., which is an apparent absurdity from the positions of classic thermodynamics.

Thermokinetics figures out an escape from the situation offering a more general method to find motive forces as derivatives of the system energy. In this case the terms of the second sum in (2.5.9) may have different sign depending on whether the system itself does work ($\boldsymbol{X}_i \cdot d\mathbf{Z}_i > 0$) or work is done on the system ($\boldsymbol{X}_i \cdot d\mathbf{Z}_i < 0$). This liberates from whatever violence against thermodynamics when applying equation (4.1.4) to bio-systems consuming the free energy (inergy) from the environment.

A significant advantage thermokinetics offers is the possibility to find from its equations the resultant $\mathbf{F} = \Sigma_i \mathbf{F}_i$ of forces of various nature, which allows to directly obtain the simplest diagonal form of kinetic laws (2.6.11) with a minimal number of the transfer coefficients $\bar{K}_{ij}$ therein.

In particular, with temperature and pressure being constant the laws of passive transport of the k^{th} substances in the finite-thickness biological membranes become:

$$J_\kappa = L_k(X_\kappa)X_\kappa = - L_k\, \Delta\zeta_k. \qquad (16.2.1)$$

Here $X_\kappa = -\Delta\zeta_k$ – diffusive potential differential across the membrane; L_k – osmotic diffusion coefficients for the k^{th} substances depending on the fields of temperature, pressure and concentration of all independent components of the system. This relationship means that transfer equations (16.2.1) are non-linear since these fields themselves and the field-conditioned coefficients L_k vary with the $\mathbf{X}_\kappa$ variation. However, with the diagonal form of laws (16.2.1) this non-linearity does not anymore impede the determination of superposition effects. Let us show this by an example of the filtration and osmotic diffusion of the k^{th} substances running simultaneously in a biological membrane. In this case the bulk (filtration) flow $\mathbf{J}_\text{v}$ and the flows $\mathbf{J}_\kappa$ of the k^{th} substances are interrelated ($\mathbf{J}_\text{v} = \Sigma_k \upsilon_k \boldsymbol{J}_\kappa$). This is especially evident for a binary system where only one of the flows is independent (say, the solvent flow $\mathbf{J}_v = \upsilon_1 \mathbf{J}_1$). This flow is caused by the solely motive force $\mathbf{X}_\kappa = -\Delta\zeta_k$. Using the expression for the exact differential of this potential (see 14.3.5) law (16.2.1) may be written as:

$$J_\kappa = - L_k[\Sigma_k \mu_{k\ell}\, \Delta c_\ell + (s_{k\text{o}} - s_k)\, \Delta T + \upsilon_k\, \Delta p]\ , \qquad (16.2.2)$$

where $\mu_{k\ell}$ – abridged symbol for the derivative $(\partial\zeta_k/\partial \text{c}_\ell) = (\partial\mu_k/\partial \text{c}_\ell)$. From here at $T = \text{const}$, $\mathbf{J}_\kappa = 0$ the stationary effect of osmotic pressure generation $\Delta\pi_\text{s}$ follows as:

$$(\Delta\pi_s/\Delta c_2)_{\text{ст}} = -(\partial\mu_\ell/\partial c_2)/\upsilon_1, \qquad (16.2.3)$$

where $\Delta c_{2\text{st}}$ – stationary differential of impurity concentrations on both sides of the membrane. This expression allows using in (16.3.3) the experimentally found value – $\Delta\pi_s$ $(\upsilon_1\Delta c_2/\Delta c_{2\text{ст}})$ instead of the value $(\partial\mu_\ell/\partial c_2)\Delta c_2$ which is hard to measure. In this case the laws of filtration and osmotic diffusion in biological membranes will become as proposed earlier (A. Katchalsky, P. Curran, 1967):

$$\mathbf{J}_v = L_v(\Delta p - \sigma_c\Delta\pi_s); \qquad (16.2.4)$$

$$\mathbf{J}_\kappa = L_k(\Delta p - \sigma_c\Delta\pi_s), \qquad (16.2.5)$$

where $\sigma_c = \Delta c_2/\Delta c_{2\text{ст}}$ – the so-called selectivity factor.

As can be seen here, due to the diagonal form (16.2.1) of the active transport laws representation, the flow integration effects in such processes can be found without Onsager's symmetry conditions (4.1.7) or without more general differential reciprocity relationships (4.5.3). However, it is even more important that these effects can be expressed exclusively in terms of the thermodynamic variables. This allows proposing a new method to determine the hard-to-measure thermodynamic parameters based on measuring the stationary superposition effects. In particular, by experimentally measuring the value $\upsilon_1(\Delta\pi_s/\Delta c_2)_{\text{st}}$ the non-calculable concentration behavior of chemical potential $(\partial\mu_1/\partial c_2)$ can be found from the relationship (16.2.3).

16.3. The Role of External energy in Vital Activity of Biosystems

Despite the noticeable successes in interpreting the laws of bio-system function from the positions of TIP and synergetics (A. Rubin, 1964; S.R. Keplen, E. Essig, 1968; L. Blumenfeld, 1977; I. Prigogine, 1977; A.K. Pritz, 1980; D. Nickols, 1985; G. Edsol, H. Gotfrend, 1986; G. Gladyshev, 1988, and others), finding a solution to the evolution problems on the rigorous physics-mathematical basis encounters considerable difficulties. The major part of them is attributed to the fact there are no potential state functions in open systems, which variation could serve as quite general and rigorous criteria of the development (ontogenesis) and evolution (phylogenesis) pertaining to bio-systems. The entropy S is inapplicable here since in the bio-systems exchanging substance with the environment it can vary due to heat transfer or mass transfer and, on the contrary, remain invariable providing the withdrawal of the system from equilibrium or its approaching this is caused by useful work done. As known from classic thermodynamics, a system can be drawn off equilibrium by only doing useful work on the system, which relates to adiabatic effects and, in principle, can not change the entropy of the system. The so-called entropy "production" $P = d_iS/dt$ does not either meet these requirements since this criterion features the minimum in only a quite particular case of stationary processes in linear systems and states in the vicinity of equilibrium (I. Prigogine, 1947), whereas the evolution processes are in principle non-stationary and mostly obey exponential (non-linear) laws. Ultimately, in all cases of useful work done on a bio-system the flows $\mathbf{J}_i$ appear to be directed against the thermodynamic forces $\mathbf{X}_i$, while the production $\mathbf{X}_i \cdot \mathbf{J}_i$ becomes negative. When these forces and flows are derived from TIP based on the expression of entropy generation rate (see 4.1.4), the share of the terms $\mathbf{X}_i \cdot \mathbf{J}_i$ in the entropy generation takes negative sign too. It is usually interpreted as a consequence of the "negentropy" inflow to the bio-system, which results in perverting the physical meaning of bio-system ordering processes and in construing it as a consequence of "order arising from chaos" rather than acknowledging the evident fact of ordered energy inflow to bio-systems from outside. The fact there are no potential state functions in thermodynamic of open systems restricts the application of the thermodynamic potentials method to biological, ecological, cosmological, etc. systems. Thermokinetics enables a solution to this problem by introducing the concept of the external (ordered) energy E as a function of the external coordinates $\mathbf{R}_i$ for a spatially heterogeneous system. This characteristic state function generalizes the notion of exergy as the maximal work a system can do before thermodynamic equilibrium with the environment has been set (J. Szargut, R. Petela, 1968; A. Andrushchenko, 1975, and others). From unifying the object of investigation with its environment in a single non-equilibrium whole and representing the ordered energy as a function of state variables for such an "extended" system the external energy becomes the most general measure of useful external working capacity of open and closed, simple and complex, homogeneous and heterogeneous systems. Let us consider the additional possibilities ensuing from the notion of the external energy E introduced as the convertible part of energy for a spatially heterogeneous system and the most general measure of how far it stands from equilibrium. First of all, let us show that the working capacity function in terms of energy carrying flows in the form of (11.1.2) enables a shorter way to obtain the same results as exergy in its traditional interpretation.

Let us assume an available heat Q well with a constant temperature of T_1, and the environment with a temperature of T_0 as a heat sink of so large capacity that the entropy flow does not change its intensive parameters. The power of the heat engine using such energy well can be found from equation (11.1.2). The entropy flow $I_s^e = dS/dt$ thru the heat engine is related with the heat flow at its inlet $I_q = \text{đ}Q/dt$ simply as $I_s^e = I_q/T_1$. In this case, integrating (11.1.2) over a temperature interval of $T_1 - T_o$ and assuming I_s^e = const (which is equivalent to assuming reversibility of Carnot heat engine based on these heat wells) gives:

$$N_q = -\int (J_q/T_1)dT = (1 - T_o/T_1)\, \text{đ}Q/dt, \qquad (16.3.1)$$

which corresponds to the expression for heat well exergy (A. Andrushchenko, 1975) $W^e_{max} = Q(1 - T_o/T_1)$.

Similarly the exergy of working medium can be expressed taking into account that in this case a substance well with a chemical potential of μ_1 exchanges not only the mass M with the environment (the mass flow $J_m^{\text{т}} = dM/dt$), but also the entropy S so that the energy converter power is derived as the sum:

$$N_T = -\int J_m^{\mathrm{e}} d\mu - \int J_s^{\mathrm{e}} dT\,. \qquad (16.3.2)$$

Integrating this expression over temperature and chemical potential intervals of $T_1 - T_o$ and $\mu_1 - \mu_o$, respectively (где $\mu_1 = h_1 - T_1 s_1$; $\mu_o = h_o - T_o s_o$) gives:

$$N_T = [(h_1 - T_1 s_1) - (h_o - T_o s_o)]\, dM/dt, \qquad (16.3.3)$$

which corresponds to the expression for working medium exergy (A.Andrushchenko, 1975) $W^e_{max} = H_1 - H_o - T_o\,(S_1 - S_o)$. Similarly the chemical exergy of reacting systems can be found.

The identity of the results obtained based on both interpretations of the working capacity function is caused by the fact that these interpretations refer to the same value. However, unlike exergy, expressions (16.3.1) and (16.3.3) derive the value of work maximum possible and with system parameters inconstant. Thus the concept of external energy is a further generalization of the exergy concept. This imparts all advantages of the characteristic state function to external energy. First of all, its value as a state function does not depend on the path the system comes to equilibrium. This excuses from the necessity to invent the ways of system reversible state-to-state transfer, which was characteristic for any working capacity functions in classic thermodynamics.

Furthermore, the ordered energy (inergy) E of an extended system is expressed directly in terms of the energy carrying flows and the thermodynamic forces $\mathbf{X}_i$. Due to this, it can be found under the boundary conditions set by the flows $\mathbf{J}_i$ or forces $\mathbf{X}_i$, i.e. similar to those in the heat-mass transfer theory. One more advantage of the external energy is that it may be differentiated by the degrees of freedom of the system. It is important also that, unlike Gibbs or Helmholtz energy, the decrease of the ordered energy E defines the useful work value at any process conditions (not only at T,p = const or T,V = const). This further extends the sphere of application of the thermodynamic potentials method. Due to all these merits the ordered energy is one of the most universal thermodynamic potentials.

Ultimately, exergy, being a state function of the system under investigation itself (regardless of the environment), is irreplaceable under the necessity to define the "reserve" of the system reversible energy in the absence of a heat/substance "inflow from outside". This is quite important when defining the external energy of an "independent" system not needing the environment to be used. The external energy in this case allows estimating the reserve of the ordered energy per each of its components $E_i = \mathbf{X}_i \cdot \mathbf{Z}_i$. This facilitates the analysis of system energy form-to form conversion.

To illustrate the universality of the ordered energy as an equilibrium and stability criterion, let us use the expression for its exact differential (see 2.3.7). To enable a more convenient comparison of the results with those already known, it makes sense to use the specific values ε_i of ordered energy and to express the specific work w_i in terms of thermostatic variables. Since according to (2.5.8) the forces $\mathbf{x}_i = -\nabla\psi_i$, while the variation of the specific distribution moments $\mathbf{z}_i$ in distribution processes $d\mathbf{z}_i = \theta_i d\mathbf{r}_i$, then for the general case of non-stationary processes the elementary work becomes:

$$-d\varepsilon_i = đw_i = \mathbf{x}_i \cdot d\mathbf{z}_i = -\theta_i d_r\psi_i, \tag{16.3.4}$$

where $d_r\psi_i = (d\mathbf{r}_i \cdot \nabla)\psi_i$ – variation of the potential ψ_i in the direction of the energy carrier Θ_i[1] transfer.

In this case the equilibrium and stability criteria for a system with any degree of freedom become, respectively:

$$\delta\varepsilon_i = -\theta_i d_r\psi_i = 0, \; \delta^2\varepsilon_i = -(\partial\theta_i/\partial_r\psi_i) > 0. \tag{16.3.5}$$

Let us use this expression to set particular equilibrium and stability conditions for various systems. For a particular case of mechanical degree of freedom $\Theta_i = -\upsilon$, $\psi_i = p$. From this it follows that at equilibrium the pressure in all points of the system is the same ($\nabla p = 0$), while $(\partial\upsilon/\partial_r p) < 0$, i.e. the gas specific volume decreases with the pressure rise. It is easy to see that these conditions are equivalent to the mechanical equilibrium and stability conditions well-known in classic thermodynamics (I.P. Bazarov, 1991). Similarly for the thermal degree of freedom ($\theta_i = s$, $\psi_i = T$) we have $\nabla T = 0$, $(\partial s/\partial_r T) > 0$, which means the same temperature all over the system and entropy rise with temperature. The electrostatic equilibrium conditions are the like $\nabla\varphi = 0$, $(\partial\theta_e/\partial_r\varphi) > 0$ meaning the same electrostatic potential φ all over the conductor and charge increase with electric potential.

Let us now consider the conditions of material equilibrium, i.e. the equilibrium distribution of the k^{th} substance among system parts. Proceeding, as usually, from Gibbs relationship (4.5.1) gives the potential of the k^{th} component as its chemical potential μ_k. In this case the material equilibrium conditions become $\nabla\mu_k = 0$, which corresponds to Gibbs conditions $\mu_k' = \mu_k''$. However, given heat and bulk mixing effects, the component potential at $p, T =$ const is the diffusion potential ζ_k (Chapter 9). In this case the Gibbs material equilibrium conditions give place to the equality of diffusion potentials $\zeta_k' = \zeta_k''$.

The phase equilibrium conditions are substantially the same, but demanding diffusion potential differential comes to zero rather than gradient

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1) Such is, in particular, the expression for the useful work of gas in stream $đw_p^e = -\upsilon d_r p$, where $\theta_i = \upsilon$ (gas volume transferred), $\psi_i = p$ (gas pressure).

(due to the system discontinuity). Thus the material and phase equilibrium is understood as the equality of diffusion potentials on the interface of subsystems. It is significant that the heat and bulk mixing effects at phase transitions are in this case construed as phase transition heat and work (like the evaporation heat and the expansion work at vaporization).

Thus all equilibrium and stability conditions known in thermodynamics may be found from the extreme of only one state function – the system external energy. Another advantage of this criterion consists in its applicability to open and closed, isolated and non-isolated, homogeneous and heterogeneous, simple and complex systems regardless of the set of thermostatic variables accepted as independent.

The method of equilibrium conditions definition based on external energy is not only straighter and shorter than that based on the max entropy principle. As follows from equilibrium conditions (4.6.6), the equality of pressures, as well as chemical, electrical and other potentials at equilibrium takes place only subject to condition (4.6.7) $T' = T''$. The conclusion usually drawn from this is the thermal equilibrium conditions are of a more fundamental importance as compared with others [1]. It is commonly stated, in particular, that material equilibrium can not set in, as a matter of fact, unless the thermal equilibrium conditions are met since a "heat-impermeable membrane is simultaneously also a mass-impermeable one" (R. Haase, 1964). This conclusion is rebutted by the experiments on annealing of welded diffusion pair (see Chapter 12), which prove that the flow of one of the movable components can cease even in the absence of thermal equilibrium. Besides, with internal processes (e.g., diffusion mixing processes) under consideration, whatever membranes are absolutely unnecessary. The apparent independence of the $\mathbf{Z}_i$ and $\mathbf{Z}_j$ parameters in equilibrium criterion (2.5.12) unambiguously evidences that the conditions of partial equilibrium of one (the i^{th}) kind are independent on equilibrium of other (the j^{th}) kind and thus rebuts the sentential opinion of a specific role of thermal equilibrium.

One more advantage of external energy consists in the fact that the stable equilibrium can be distinguished from the metastable (relatively

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[1] Note this conclusion ensues from construing entropy not as an independent variable (as by Clausius), but rather as the state function $S = S(U,V,\Theta_i)$ varying with the system energy in adiabatic processes (V,Θ_i = var). Such an extrapolation of the entropy concept, if unheeded, causes a number of confusions.

stable) equilibrium and the labile (absolutely unstable) one. Equilibrium for the metastable state can be disturbed only at finite variations of the system parameters $\Delta\theta_i$ и $\Delta\mathbf{z}_j$

$$\delta^2\varepsilon_i = -(\partial\mathbf{x}_i/\partial\mathbf{z}_i) > 0 \text{ при } \Delta\theta_i, \Delta\mathbf{z}_j \neq 0, \varepsilon_i > 0, \qquad (16.3.6)$$

while for labile states – at infinitesimal variations of the system parameters:

$$\delta^2\varepsilon_i = -(\partial\mathbf{x}_i/\partial\mathbf{z}_i) > 0 \text{ при } d\theta_i, d\mathbf{z}_j \neq 0, \varepsilon_i > 0. \qquad (16.3.7)$$

For whatever process to arise in a system being in a retarded or metastable equilibrium, some “energy barrier” has to be overcome. Such a “barrier”, as a matter of fact, exists for most of the forms of energy. For the thermal form of energy it shows in a certain temperature difference to be generated (e.g., a certain overheating or overcooling of one of the phases to initiate phase transition); for mechanical motion of bodies – in overcoming the static (rest) friction; for chemical and bio-chemical processes – in supplying “activation energy”; for spontaneous fission of uranium heavy nuclei – in introducing fast neutrons to enough amount; for thermonuclear reactions – in raising heat up to tens million degrees, etc. The value of such a barrier (its exergy) is allowed for in kinetic equations by introducing a “threshold” force value of F_{io}, below which the process fails to arise.

With introducing the external energy concept it becomes also absolutely clear that the forms of the energy supplied to a system and accepted by the system are different things. It becomes clear that not only the form (ordered or disordered) of energy *supply* to a system is a matter of importance, but also *how* the energy has been *accepted* by the system. In particular, supply and abstraction of dissipation heat (disordered energy) can change the external energy of a system in the same way as the work done on the system. A body may be, e.g., non-uniformly cooled. Then parts (subsystems) will appear therein having different temperatures and capable to serve as heat wells and heat sinks. Such a body will acquire an ability to do useful external work before thermal equilibrium has set in there. The form itself of accepting by a system the energy supplied from outside is, to a great extent, defined by the system properties, i.e. by the forces the system will set against the external action. If these are forces with a resultant of $\mathbf{F}_i$, the supplied energy will, at least partially, be accepted by the system as ordered work done on it. Such is, e.g., the radiant energy partially consumed for photosynthesis of plants, while partially (within the thermal radiance range) accepted as heat. With the resultant force absent, the system will accept an external action as disordered work. This work can replenish only the equilibrium part of the system energy, viz. the anergy. All the said refer to not only technical, but also biological systems since their vital activity is based on the external work they do.

16.4. Maximum of inergy as Maturity Criterion for Bio-Organisms

Biological objects relate to the category of open systems developing due to interchange with the environment of rather substance than energy. These are the metabolism processes (substance exchange) associated with chemical reactions running in bio-systems that are a well of the ordered energy they dispose of.

At the same time the processes of energy conversion in non-equilibrium bio-systems bear their own specific character. Though in each of the elements on the surface of the cell membrane these processes, as it has already been mentioned, bear the vector (directional) character, it is impossible to define a direction predominant for the whole set of the cells comprising the organism. This means that chemical reactions for a bio-system as a whole bear the scalar character. In this case the general measure of how far this bio-system stands from equilibrium and the main source of its vital activity is its internal ordered energy (inergy) E represented in (2.3.6) in terms of the deviation of the system general potentials Ψ_i from their equilibrium values $\bar{\Psi}_i$. The value of inergy may be found directly from known fields of temperatures, pressures, concentrations, etc. both for the system as a whole and for each of ith degrees of its freedom. This makes the inergy one more feasible and extremely "physical" criterion of how far any system (including a bio-system) stands from equilibrium.

To define within the energy of some system E the non-equilibrium (convertible) part associated with heterogeneous reactions, let us apply to relationship (16.1.1). According to it the equilibrium concentration of the kth substance = $\bar{c}_k$ (at $\xi_r = 1$) is equal to = $\bar{c}_k = c_{ko} + \Sigma_r \nu_{kr}$. Substituting this expression into relationship (16.1.1) gives:

$$c_k = \bar{c}_k - \Sigma_r\, \nu_{kr}\,(1 - \xi_r). \qquad (16.4.1)$$

Multiplying (16.4.1) by μ_k and summing over all k^{th} components easily gives an expression for the chemical potential μ_m of mixture (Gibbs specific energy):

$$\mu_c \equiv \Sigma_k \mu_k c_k = \Sigma_k \mu_k \bar{c}_k + \Sigma_r \mathrm{A}_r (1 - \xi_r). \tag{16.4.2}$$

This expression represents the Gibbs specific energy as a sum of the equilibrium $\Sigma_k \mu_k \bar{c}_k$ and non-equilibrium $\Sigma_r \mathrm{A}_r(1- \xi_r)$ components. These components describe independent processes since mass transfer simultaneously and equally changes both c_k and $\bar{c}_k$ leaving the ξ_r invariable, whereas chemical reactions, on the contrary, change the coordinates ξ_r, while leaving the = $\bar{c}_k$ invariable. Note by the way that the last term in (9.1.4) is different from zero insofar as the chemical potentials μ_k of the reagents being introduced into the system are unequal to their equilibrium values $\bar{\mu}_{ik}$ (at $\xi_r = 1$). Thus in locally non-equilibrium systems both equilibrium and non-equilibrium parts of the Gibbs energy $G = \Sigma_k \mu_k M_k$. (sometimes termed as chemical energy of the system under consideration) may be distinguished. Multiplying the Gibbs chemical energy by the mass of the k^{th} substance $M_k = \Sigma_r M_{kr}$ and introducing (to make the description general) $Z_r = M\nu_{kr}(1 - \xi_r)$ as the coordinate of the r^{th} reaction gives:

$$U_x = \Sigma_k \mu_k \bar{M}_k + \Sigma_r \mathrm{A}_r Z_r\,. \tag{16.4.3}$$

Thus the energy of media chemically reacting may also be resolved into the non-equilibrium (convertible) part which, according to the classification herein adopted, should be termed as the *chemical inergy*

$$E_{ch} = \Sigma_r E_r = \Sigma_r \mathrm{A}_r Z_r\,, \tag{16.4.4}$$

and the equilibrium (inconvertible) part of this energy, i.e. the *chemical anergy*:

$$\bar{U}_{ch} = \Sigma_k \mu_k \bar{M}_k\,. \tag{16.4.5}$$

The chemical inergy of a system features its convertible part regardless of what this energy conversion will be – dissipative or useful (convertible).

The latter means doing useful internal work, i.e. conversion of some forms of chemical inergy into other forms necessary to provide the vital activity. This is the specific character of bioenergetics. Strictly speaking, chemical reactions are also caused by spatial heterogeneity in distribution of atoms in chemical elements within chemical compounds. Chemistry in this sense has always been a science of substance restructuring. This process has the vector character when referred to molecular level. However, at macro-level a chemical reaction acquires the scalar character due to the chaotic arrangement and motion of all set of atoms and molecules.

Substance restructuring processes are a peculiar analog of chemical reactions. A convertible (useful) component available in these processes, differs them from the non-equilibrium phase transitions of the 1st kind, i.e. the substance restructuring processes imply a transition of some kind of energy to not only heat (anergy), but also to inergy of other kind. Such are, in particular, the processes of biological structures formation sometimes termed as “self-assembly” (G. Gladyshev, 1976).

It can be easily seen that the inergy E_{ch} possesses all properties of the characteristic state function. Its decrease defines the work being done in the course of the chemical reaction:

$$-dE_{ch} = \Sigma_r \mathrm{A}_r d\xi_r\,. \qquad (16.4.6)$$

Thus the inergy possesses potential properties. Unlike Gibbs energy, using the chemical inergy does not require the process character identification (p, T = const). Furthermore, the derivative of Y_x with respect to the reaction coordinate Z_r, according to (16.4.4), defines the motive force of the reaction – its affinity:

$$\mathrm{A}_r = (\partial E_{ch}/\partial Z_r). \qquad (16.4.7)$$

The inergy-based method of chemical equilibrium conditions definition

$$(\partial E_{ch}/\partial\lambda_r) = 0,\ \mathrm{A}_r = 0, \qquad (16.4.8)$$

is straighter and shorter than that based on max entropy since does not require constancy of the equilibrium parameters Θ_i. This also refers to using inergy as the system stability criterion

$$\delta^2 E_{ch} = -(\partial \mathrm{A}_r/\partial \xi_r) > 0\,. \qquad (16.4.9)$$

One more advantage of inergy consists in the fact that the true equilibrium $E_{ch} = 0$ can be distinguished from the so-called “retarded” equilibrium (when chemical conversions cease because of the absence of enzymes or catalysts), as well as from the “metastable” (relatively stable) equilibrium and the “labile” (absolutely unstable) one. These states differ from the true (full) equilibrium in their inergy that exceeds zero ($E_{ch} > 0$), but may decrease if some “activation energy” is supplied to the system. Such an “energy barrier”, as a matter of fact, exists for most of the forms of energy. For the thermal form of energy it shows in a certain temperature difference to be generated (e.g., a certain overheating or overcooling of one of the phases to initiate phase transition); for mechanical motion of bodies – in overcoming the static (rest) friction; for chemical and bio-chemical processes – in supplying “activation energy”; for spontaneous fission of uranium heavy nuclei – in introducing fast neutrons to enough amount; for thermonuclear reactions – in raising heat up to tens million degrees, etc.

Availability of such criteria substantially extends the applicability of the thermodynamic potentials method to bio-systems. Let us consider an example of the inergy applied to develop the maturity criterion for organisms in ontogenesis. Bio-systems are known to be developing by two ways – extensive and intensive (D. Lourier, H. Vagensberg, 1984). In the first case, which is characteristic, e.g., for plankton populations, the inergy flow the bio-mass consumes tends to a peak value the particular environment conditions. In the second case, which is characteristic rather for living organisms, the unit consumption (by bio-system mass or volume) of the free energy (inergy) from the environment increases in the process of phylogenesis due to a more perfect structure of the system and a more effective energy conversion in it. The working

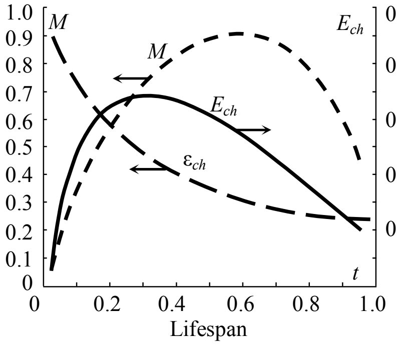

Fig.16.2. inergy as Maturity Criterion for Bio-Organisms

capacity of an individual living organism adequately depends on its total mass and specific working capacity. Since the mass M of a living organism increases, whereas the specific working capacity (per unit of mass) decreases with its age due to senescence, the total working capacity of a particular living organism as the production of the above two parameters most exactly corresponds to the concept of its maturity in ontogenesis (E. Laifut, 1977, E. Rudakov, 1978) 1).

This statement is illustrated by curves on Fig.16.2 showing the mass *M* of a living organism, its specific inergy γ_x and its total inergy $E_{ch} = M\varepsilon_{ch}$ related to max values and plotted against the relative lifespan. The mass of a living organism is known to be increasing with its development, reaching a maximum followed by gradual decreasing till its death due to dewatering of living tissues (G. Gladyshev, 1988). As for the specific inergy, this value, like the Gibbs specific free energy, steadily decreases in full compliance with the second law of thermodynamics due to the composition modification of bio-tissues. Because of such a behavior of the above curves the total inergy of the system E_{ch} reaches its maximum much earlier than the mass. The last fact has been verified in multiple observations and may be considered as a strictly ascertained fact.

16.5. Unity of Technical and Biochemical Energy Converters

The investigation of muscular chemical-into-mechanical energy converters in a number of guidelines on bioenergetics is based on the TIP provisions formally applied to bio-systems (S. Keplen, E. Essig, 1968; A. Rubin, 1984). In this connection the kinetic equations of metabolism and energy conversion processes in muscular movers are expressed in the form of Onsager's linear phenomenological laws (5.1.6) wherein the flows $\mathbf{J}_i$ and forces $\mathbf{X}_j$ are derived from the expression for the entropy generation rate (see 4.1.4). This looks quite logic until the investigator encounters the efficiency ambiguity for such converters showing in the fact that according to (4.1.4) the entropy generation may be resolved into the components $\mathbf{J}_i\mathbf{X}_i$ and $\mathbf{J}_j\mathbf{X}_j$ voluntarily (S. De Groot, R. Mazur, 1964). In fact, the only TIP

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1) It is relevant to note that using the concept of inergy is very promising for estimate of "buffering capacity" and "ecosystem development degree".

requirement when choosing flows and forces is that the total entropy generation be maintained (invariance of dissipation function (5.3.3) characterizing the dissipation power). Doubts in the TIP applicability grow even stronger when the different-kind forces $\mathbf{X}_i$ and $\mathbf{X}_j$ relate to the same (even or odd) time functions. In this case the Onsarer's (but nor Cazimir's) symmetry conditions must be observed, for which the requirement the matrix of phenomenological coefficients to be positively defined is expressed as the restriction $(R_{ij}+ R_{ji})^2 < 4R_{ii}R_{jj}$. In this case, as will be shown in Chapter 11, the efficiency of any (including biological) energy converters can not be in excess of about 17.5%, which does not naturally occur in reality. The point is that in the energy conversion processes, unlike the energy transfer, the different-kind flows $\mathbf{J}_i$ and $\mathbf{J}_j$ are interrelated. This relation can be revealed based on the law of energy conservation in the form of (2.6.9), wherefrom it follows that at stationary conditions with reversible conversion of the i^{th} form of energy into the j^{th} form the power at the converter input and output is the same:

$$\mathbf{X}_i \cdot \mathbf{J}_i = - \mathbf{X}_j \cdot \mathbf{J}_j \, . \tag{16.5.1}$$

The said interrelation complies with the differential reciprocity relationships which for energy conversion processes are of invariably anti-symmetrical character:

$$\partial \mathbf{J}_i / \partial \mathbf{X}_j = - \, \partial \mathbf{J}_j / \partial \mathbf{X}_i \, . \tag{16.5.2}$$

Such a character of the reciprocity relationships is caused by opposite sign of the work done by the forces $\mathbf{X}_i$ and $\mathbf{X}_j$ and does not depend on whether they are even or odd time functions (i.e. on the anti-symmetry conditions Cazimir stated proceeding from the static-mechanical considerations). This anti-symmetry is of principal importance as resulting in opposite sign of the terms in the phenomenological laws of energy conversion, which under linear approximation become:

$$\mathbf{J}_i = L_{ij} \, \mathbf{X}_i - L_{ij} \, \mathbf{X}_j \, . \tag{16.5.3}$$

$$\mathbf{J}_j = L_{ji} \, \mathbf{X}_i - L_{ji} \, \mathbf{X}_j \, . \tag{16.5.4}$$

Unlike the Onsager's phenomenological laws, these equations express decreasing the flow $\mathbf{J}_i$ of primary energy carrier with approaching the "no- load" operation (i.e. with increasing the force $\mathbf{X}_j$ to be overcome). Therefore these are the equations which, with regard to the energy conversion, should be termed phenomenological (i.e. really experience-based) rather than Onsager-postulated laws (5.1.6).

Let us consider for example the fibril as a muscle element converting chemical energy into mechanical one. In this case the generalized rate $\mathbf{J}_i$ of the primary process is construed as the flow $\mathbf{J}_r$ of the substances taking part in this chemical reaction, while the generalized rate $\mathbf{J}_j$ of the related process – as the muscle traction rate. Each of these flows according to (16.5.3)–(16.5.4) depends on both forces, the first of which, $\mathbf{X}_i$, is now construed as the negative gradient $-\mathrm{grad}(\mathrm{A}_r\lambda_r)$ of chemical reaction affinity, while the other – the fibril contraction $\mathbf{X}_j$. Note that when the chemical reaction runs thru to the end ($\xi_r = 1$), the force $\mathbf{X}_i$ is equal to the chemical reaction affinity A_r.

Laws (16.5.3) and (16.5.4) may be more conveniently represented in dimensionless form not containing phenomenological coefficients. To do so, let us consider the so-called "isometric muscle traction" condition (analog of the engine/welding transformer no-load operation). At this condition the force $\mathbf{X}_j$ reaches its peak value $\mathbf{X}_{j\mathrm{o}}$ (no-load strength) when $\mathbf{J}_j = 0$. This condition is opposed by the so-called "unloaded muscle traction" condition (analog of the transformer secondary winding short circuit) when $\mathbf{X}_j = 0$, while $\mathbf{J}_j$ is equal to the short-circuit current $\mathbf{J}_{jk}$. Expressing $\mathbf{X}_{j\mathrm{o}}$ and $\mathbf{J}_{jk}$ according to (16.5.3) and (16.5.4) in terms of the phenomenological coefficients gives at $\mathbf{X}_i$ being constant:

$$\mathbf{X}_j/\mathbf{X}_{j\mathrm{o}} + \mathbf{J}_j/\mathbf{J}_{jk} = 1. \tag{16.5.5}$$

Such a form of the phenomenological laws still more stresses the unity of energy conversions in any forms. In a more general case of the phenomenological coefficients as some power functions of the relating forces $L_{ii} = L_{ii}(\boldsymbol{X}_j/\mathbf{X}_{j\mathrm{o}})^{\mathrm{a}}$ and $L_{jj} = \mathrm{L}_{jj}(\boldsymbol{J}_j/\mathbf{J}_{jk})^{\mathrm{a}}$, where a is an experimental value, these equations become non-linear:

$$(\mathbf{X}_j/\mathbf{X}_{j\mathrm{o}})^{1+n} = (1 - \mathbf{J}_j/\mathbf{J}_{jk})^{1+n}\,. \tag{16.5.6}$$

The character of such semi-empirical laws with a various value of the exponent $(1+a)$ equal to 1.0, 1.15, 1.3 and 1.5 is plotted on Fig.16.3 in the form of curves 1, 2, 3 and 4, respectively. As follows from the figure, at $a = 0$, the relationship $\mathbf{X}_j/\mathbf{X}_{jo}$ vs. $\mathbf{J}_j/\mathbf{J}_{jk}$ is linear (straight line 1). The higher the exponent "a" is, i.e. the stronger the dependence of phenomenological coefficients on forces is, the more non-linear the curve becomes. However, this non-linearity is caused by exclusively the non-linearity of laws (16.5.3)–(16.5.4) proper and has nothing to do with relating the rates of both processes, i.e. the flows $\mathbf{J}_i$ and $\mathbf{J}_j$ as sometimes imagined (Keplen, Essig, 1968). Let us, for comparison, consider the Hill's empirical equation which accurately enough characterizes the muscles for different kinds of animals:

$$(\mathbf{X}_j/\mathbf{X}_{jo})^{1+n} = (1 - \mathbf{J}_j/\mathbf{J}_{jk})^{1+n} . \tag{16.5.6}$$

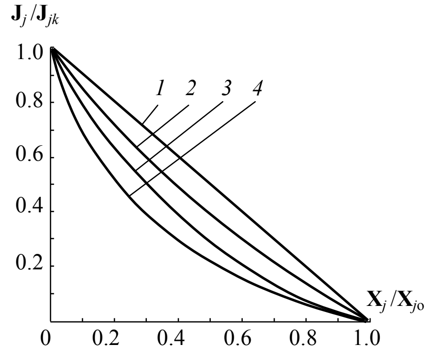

Fig.16.3. Load semi-empirical characteristics of the fibril

where $æ_o$ is a value Hill named the "efficiency index" for muscle. It is connected with the value $q_{ch} = L_{ii}/(L_{ii}L_{jj})^{0,5}$ he named the "flow relation factor" by the relationship $q_{ch} = 1/(1 + æ_o)^{0,5}$, i.e. is a function of the quality factor $æ_o = \Phi - 1$ we earlier introduced. The Hill's curves for various q_x well correspond to those plotted on Fig.16.3, i.e. the higher the flow relation factor q_{ch} is, the more non-linear the curve becomes. At the same time the curves of (16.5.6) basically differ from the Hill's curves in the interpretation of what causes the non-linearity of the phenomenological laws. By Hill the linear relationship $\mathbf{X}_j/\mathbf{X}_{jo}$ vs. $\mathbf{J}_j/\mathbf{J}_{jk}$ corresponds to the value $L_{ii}/(L_{ii}L_{jj})^{0,5} = 0$ (or $\Phi = \infty$), i.e. to the trivial case of $L_{ii} = -L_{ji} = 0$. However, the fact the relation factor becomes zero means no interrelation between the flows $\mathbf{J}_i$ and $\mathbf{J}_j$, i.e. no energy conversion itself! So the non-linearity of phenomenological laws has appeared to be connected with the muscle movers' efficiency. This fact once again confirms that TIP can not be formally exported to the processes of useful conversion of energy (V. Etkin, 1995).

Conclusions to Part 5

Even more significant are the results obtained from thermokinetic regarding the theory of transfer irreversible processes. The consistently thermodynamic ("non-hypothetic") substantiation of its fundamentals allows extending this theory to the nonlinear region and states lying far from equilibrium. Such a generalization has been reached both due to applying more general (differential) relationships of reciprocity and due to reducing the transfer laws to a simpler diagonal form not demanding the application of these relations. This has made it possible to implement a new method of analyzing superposition effects, which replaces the stationarity conditions by the partial equilibrium conditions and allows further reduction of the number of kinetic coefficients in the transfer equations from $n(n+1)$ to n. This has made it possible to set a number of new relationships between physical effects and to provide a theoretical substantiation of a number of known empirical laws.

KEY SIMBOLS

U, u – total (J) and specific (J/kg) energy of a system.

E, ε – total (J) and specific (J/kg) ordered energy (inergy).

E^{k}, E^{p} – kinetic and potential ordered energy (J).

$\bar{U}, \bar{u}$ – total (J) and specific (J/kg) unordered energy (anergy).

H, h – total (J) and specific (J/kg) enthalpy.

G, Γ – Gibbs and Helmholtz energy (J).

Φ_J, Π_X – local dissipation potentials, W

Θ_i, θ_i – total and specific generalized coordinate of the i^{th} scalar process

Ψ_i, ψ_i – generalized potential of the i^{th} scalar process and its local value; $\bar{\Psi}_i$ – the same in equilibrium state.

$\mathbf{F}_i$, $\mathbf{M}_i$ – resultant motive force (N) and torque (N·m) of the i^{th} vector process.

$\mathbf{X}_i$, $\mathbf{x}_i$ – specific thermodynamic force of the i^{th} vector process and its local value.

$\mathbf{Z}_i$, $\mathbf{z}_i$ – total and specific values of distribution moment Θ_i.

$\mathbf{v}$, $\mathbf{w}$ – absolute and relative velocity, m/s.

$\mathbf{R}_i$, R_i – displacement vector of Θ_i and its modulus.

$\mathbf{J}_i$, $\mathbf{j}_i$ – generalized velocity of the i^{th} vector process (flow) and its density

$\mathbf{J}_i^{\mathrm{c}}$, $\mathbf{j}_i^{\mathrm{c}}$ – displacement flow of the i^{th} energy carrier and its density.

W_i, w_i – total (J) and specific (J/kg) work of the i^{th} process.

$W^{\mathrm{o}}, W^{\mathrm{u}}, W^{\mathrm{D}}$ – ordered, unordered and dissipative work, J.

N – process power (capacity), W.

Q, q – total (J) and specific (J/kg) process heat.

$đQ$, $đW$ – elementary heat and work, J.

q^*, w^* – specific heat and transfer work of the k^{th} substance, J/kg.

T, T_m – local and mass mean absolute temperature, K.

$\bar{T}_1, \bar{T}_2$ – thermodynamic mean temperatures of heat supply and abstraction, K.

M, M_k – mass of a system and the k^{th} substance therein, kg.

p – absolute pressure, N/m^2.

V, υ – total (m^3) and specific (m^3/kg) volume of a system.

S, s – total (J/K) and specific (J/kg·K) entropy of a system.

υ_k, $\upsilon_{k\mathrm{o}}$ – partial molar volume of k^{th} component and molar volume of the pure k^{th} substance m^3/mol.

s_k, $s_{k\text{o}}$ – partial molar entropy of the k^{th} component and molar entropy of the pure k^{th} substance, J/mol·K.

c_p, c_v – isobaric and isochoric specific heat, J/kg·K

μ_k , $\overline{\mu}_k$ – chemical potential of the k^{th} component and its equilibrium value, J/kg.

ζ_k, $\bar{\zeta}_k$; ς_k, $\bar{\varsigma}_k$ – diffusive and osmotic potential of the k^{th} substance in current and equilibrium status, respectively.

c_k, $\overline{c}_k$ – mass fraction of the k^{th} component in its current and equilibrium status, kg/kg.

φ – electric potential, V.

ρ – density of a system, kg/m^3.

$d_\text{e}\Theta_i$, $d_u\Theta_i$ – Θ_i-elementary variations conditioned by external energy interchange and internal sources, respectively.

η_t, η_N – thermal and power efficiency.

P, σ_s – dissipative function, W/K, and density of entropy internal source, W/m^3·K.

R_{ij} – coefficients of resistance to the i^{th} flow $\mathbf{J}_i$ from the j^{th} forces.

L_{ij} – phenomenological coefficients inverse to resistances R_{ij}.

A_r – standard affinity (maximal work) of the r^{th} chemical reaction.

N_{kr} , ν_{kr} – numbers of moles and stoichiometric coefficients of the k^{th} substances in the r^{th} reaction.

ξ_r , w_r – degree of completeness and rate of the r^{th} chemical reaction.

B, Φ, – load and quality factors of a power installation.

E, $\mathbf{A}_\text{e}$ – electromotive force and vector potential.

$\mathbf{H}$ – magnetic field intensity, A/m.

$\mathbf{E}$ – electric field intensity, V/m.

$\mathbf{P}$, $\mathbf{D}$ – polarization vector and electric displacement vector of dielectric unit volume, C/m^2.

$\boldsymbol{\omega}$, $\boldsymbol{\Omega}$ – angular velocity of rotation and precession motion, 1/s.

ν, λ – radiation frequency and wavelength.

γ, t – Lorentz factor and time.

Ex,ex – total (J) and specific (J/kg) exergy of a system.

Φ – good quality criterion of machine.

B – load criterion of machine.

G_m – gas flow, kg/s.

Э – production output, W.

З_p – machine planned costs,$.

œ, ĝ – variable component of unit cost and finished product unit price, $/kg .

$\mathbf{r}$ – radius–vector of a field point.

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Contents

Part 1
THERMODYNAMICS AS THEORETICAL BASIS OF HEAT ENGINEERING

Part 2.
HEAT ENGINEERING FUNDAMENTALS

Part 3.
ELIMINATION OF NEGATIVE CONSEQUENCIES OF THERMODYNAMICS EXTRAPOLATION

Part 4
FURHER GENERALIZATION OF HEAT ENGINE THEORY

Part 5
EXTENSION OF ENERGY TRANSFER THEORY APPLICABILITY