Generalization of Onsager's Reciprocal Relations

Valentin A. Etkin
Integrative Research Institute, Haifa, Israel

Abstract: Objective of the present research is the proof of the Differential (generalized) Reciprocal Relations (DRR) between streams J_i and their moving forces X_j, more general, than Onsager-Cazimir's relations and applicable not only to relaxing systems but also to the systems making useful work independence whether they are linear or not. Object of research is most the general class of spatially non-uniform systems not submitting to hypothesis of local equilibrium and to principle of linearity and supposing simultaneous flowing in them of a thermo-mechanical, thermo-electric, thermo-chemical, electro-magnetic, thermo-galvano-magnetic, etc., processes of transfer and transformation of energy. Primary results of research is essential expansion of area of applicability of Onsager-Cazimir's reciprocal relations by their reception as consequences DRR, backgrounds of their fairness at inconstancy of basic kinetic coefficients L_{ii} and demonstrations of their applicability to processes of useful transformation of energy. In study is new more brief way of proof DRR and their universality; a conclusion to their basis of Maxwell's equations; application DRR to a finding of the diagonal form of transport laws by simplification of a method of a finding of superposition effects without use of kinetic coefficients L_{ij} in them with its propagation on non-stationary processes. The practical importance of the received results consists in generalization of methods of non-equilibrium thermodynamics in expansion of scope DRR on non-linear systems and processes with any degree of dissipativeness in a finding of the diagonal form of laws of transfer in the further reduction of number of kinetic coefficients in them from n (n+1)/2 up to n and in creation of preconditions for development the theory studying kinetics of energy transformation processes.

Key words: Non-equilibrium thermodynamics, differential reciprocal relations, prove anti-symmetric conditions, Maxwell's equations, transfer laws, processes, transformation

INTRODUCTION

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 (TIP). This field in macroscopic physics of the 20th century was named the theory of irreversible processes (Denbigh, 1951; Meixner, 1954; Fitts, 1962; De Groot and Mazur, 1962). 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. Its contribution was appreciated by two Nobel prizes awarded in the field (Onsager, 1931; Prigogine, 1947).

But this theory was based on a hypothesis of local equilibrium and a principle of a minimum of entropy production in stationary processes and consequently did not reach completeness and the severity which is peculiar to a classical thermodynamic method (Groot, 1951; Bejan, 2016; De Groot and Mazur, 1962). Besides it was limited to studying purely dissipative processes and did not

consider processes of useful transformation of the energy which are the principal object of thermodynamics (Sandler, 2017; Kondepudi and Prigogine, 2014; Ness, 2015). The last has been caused by that the basic operational values of this theory-thermodynamic forces X_i and fluxes J_i are determined in it as derivative from entropy S that does not take into consideration reversible component of real processes which as is known, does not influence it. As a result of it an vast region of processes with relative efficiency above zero fall out of TIP competency.

Meantime kinetics of those processes interests not only power engineering and energy technology for which energy transformation and are basic TIP-method are the most acceptable in principle. The thermodynamic investigation of biological systems is also impossible without useful work against equilibrium 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. All that begets a problem of enlarging TIP to include the

systems performing some useful work. In this study consistently thermodynamic decision of this problem is offered.

MATERIALS AND METHODS

The researcher has selected the thermodynamic method, leaning on properties of full differential of some functions of a condition (mainly energy). Its specific character in the given particular case consists in generalization of the basic equation of thermodynamics by introduction of missing extensive parameters of spatial heterogeneity Z_j which derivatives on time give streams J_j and thermodynamic forces X_j as derivative of energy on Z_j.

The existing quasi-thermodynamic theory of relaxation processes: 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 processes. However, the development in that direction demanded introducing in thermodynamics the transfer concepts intrinsically extraneous for it. One of these belongs to Umov who wrote the law of conservation of energy in terms of the energy flow across the stationary borders of the system. The flow concept in application to entropy 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. A little bit later De Donder related the entropy source with the rate of the chemical reactions with its affinity. That was how the concepts of flow and process rate started their introduction into thermodynamics.

Most the decisive step in this direction has been made only in 1931 by Onsager (1931). It has constructed his theory of physicochemical process rate 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 $\Theta_1, \Theta_2, ..., \Theta_n$ differ from their equilibrium values by a value of $\alpha_1, \alpha_2, ..., \alpha_n$, it is naturally to assume that the difference between the entropies of the current S and equilibrium S_o states ΔS is a some function of α_i. In this case the reason of the i th scalar process generation (the scalar thermodynamic force X_i) and the generalized rate of relaxation process (named by Onsager the flow J_i) could be found from the expression for the entropy generation rate:

$$dS/dt = \Sigma_i (\partial S/\partial \alpha_i) d\alpha_i/dt = \Sigma_i X_i J_i \qquad (1)$$

Where:

$$X_i \equiv (\partial S/\partial \alpha_i); \ J_i \equiv da_i/dt$$

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:

$$J_i = \Sigma_j L_{ij} X_j \times (i, j = 1, 2, ..., n) \qquad (2)$$

Onsager referred to those laws of relaxation processes as well as the associated coefficients L_{ij} as "phenomenological" (i.e., practice-based). Such a (matrix) form of kinetic equations differed from Fourier's, Ohm's, Fick's, Darcy's, etc., laws by the presence of additional terms (with subscripts $i \neq j$). The non-diagonal summands in expression (Eq. 2) 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 "non-diagonal" phenomenological coefficients L_{ij} and L_{ji} ($i \neq j$) was most important in the Onsager's theory:

$$L_{ij} = L_{ji} \qquad (3)$$

These symmetry conditions are called the reciprocal relations. 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. Onsager obtained those famous 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 These three statements outstep the framework of thermodynamics. Therefore, he named it "quasi-thermodynamics". Onsager was afterward awarded the Nobel Prize for his studies in that field. Those studies attributed to non-equilibrium thermodynamics just as much as the R. Clausiu's 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. Casimir (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 (Eq. 6) would go over into the anti-symmetry conditions:

$$L_{ij} = -L_{ji} \qquad (4)$$

A little bit later Prigogine (1947) 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). That allowed further solving a number of problems associated with the evolution of non-equilibrium systems.

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. 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 (Etkin, 2010) which unlike W. Thomson's "pseudo-thermostatics" in 1882 and L. Onsager's "quasi-thermodynamics" in 1931 would not "un-file" reversible or irreversible part of real processes but would cover the entire of its spectrum. For this purpose it is necessary to pass to a finding of forces X_i, X_j and flows J_i, J_j on more general basis supposing both increase and decrease of energy of system.

RESULTS AND DISCUSSION

Generalization of irreversible thermodynamics on the systems making work: It is known that in thermodynamics full energy is subdivided on internal U and external E. The first depends on internal variables Θ_i (entropy S, Volume V, mass of kth substances M_k, charge 3, etc.), i.e., $U = U (\Theta_1, \Theta_2, ..., \Theta_n)$. The second depends on position of system as the whole concerning an environment, i.e. from radius-vector r of the center of these values, i.e., $E = E (r_1, r_2, ..., r_m)$. It means that full energy of system as function of its condition looks like $\ni = \ni (\Theta_i, r_j)$ and they exact differential be expressed by the following identity (Groot and Mazur, 2013).

$$d \ni \equiv \Sigma_i \psi_i d\Theta_i - \Sigma_j F_j \cdot dr_j, \begin{pmatrix} i = 1, 2, ..., n; \\ j = 1, 2, ..., m \end{pmatrix} \qquad (5)$$

Where:

$\psi_i \equiv (\partial \ni / \partial \Theta_i)$ = The generalized potentials such absolute temperature T and absolute pressure p, chemical, electric, etc., potential

$F_i \equiv -(\partial \ni / \partial r_i)$ = Forces in their usual (newtonian) meaning

n, m = The number of the scalar and vector coordinates describing a condition of system

The fundamental identity (Eq. 5) represents result of joint definitions of parameters ψ_i, Θ_i and F_j, r_j and consequently is valid regardless of what causes the variation of the parameters Θ_i and r_j either the external energy exchange or the internal (including relaxation and anti-relaxation) processes. Last is made against equilibrium in system in processes 'ascending diffusion' active transport in biosystems, polarization of substances, self-organizing of systems, etc. Therefore, Eq. 5 is applicable to any processes (both reversible and irreversible). The work described by second sum of Eq. 4 may be external or internal (depending on where the forces arise either in the system itself or outside) useful or dissipative (depending on what the work involves either purposeful conversion of energy or its dissipation); long-range or short-range (depending on radius of action); mechanical, thermal, electrical, chemical, etc., (depending on nature of the forces to overcome).

Thus research dW_j^e any jth sort, described by members of second sum (Eq. 5), maybe expressed as through usual forces F_j and replace d r_j and through parameters of non-equilibrium state X_j and Z_j:

$$dW_j^e = \Sigma_j F_j \cdot dr_j = \Sigma_j X_j \cdot dZ_j \qquad (6)$$

Expression (Eq. 5) can be copied in the form, containing full derivatives on time t from parameters of system:

$$d \ni /dt \equiv \Sigma_i \ \psi_i \ d\Theta_i /dt - \Sigma_j F_j \cdot v_j \qquad (7)$$

Here, $v_i = dr_j/dt$ the generalized speed of jth process connected with common concept of a vector stream J_j of value Θ_i by a simple parity $J_j = \Theta_j v_j$. Owing to this generality and the concept of thermodynamic force X_j gets uniform sense of specific force $X_j = F_j/\Theta_i$ and expression $X_j.J_j$ capacityes of jth process $N_j = X_j.J_j = F_j.v_j$. Owing to such method of a finding of streams J_j and forces X_j they get uniform sense, uniform analytical expression and a uniform way of a finding.

Unlike expression (Eq. 1) where work X_iJ_i is especially positive, in expression (Eq. 6) capacity N_j maybe both positive and negative that conforms to fulfilment of work or system or above system. It does an assessment of efficiency of varied converters of energy quite unequivocal, allows to distribute the theory of actual processes to processes of useful transformation of energy (Etkin, 2010).

The proof of differential reciprocal relations: From Eq. 5 on the basis of the theorem about independence mixed derivative from the order of differentiation $(\partial^2 \ni /\partial r_i \partial r_j = \partial^2 \ni /\partial r_j \ \partial r_i)$ follows:

$$\left(\partial F_i /\partial r_j \right) = \left(\partial F_j /\partial r_i \right) \qquad (8)$$

This differential parity of thermodynamics can be expressed in the generalized speeds of processes as $d \ r_j = v_j dt$ and $dr_i = v_i dt$. Then after reduction dt instead of (Eq. 7) it is possible to write:

$$\left(\partial F_i /\partial v_j \right) = \left(\partial F_j /\partial v_i \right) \qquad (9)$$

Parity (Eq. 9) can be expressed in terms of thermodynamic forces X_i, X_j and streams J_i, J_i:

$$(\partial X_i /\partial J_j) = (\partial X_j /\partial J_i) \qquad (10)$$

These parities have been received by us earlier in more complex way and named by differential reciprocal relations (Etkin, 1989). Rysselberghe (1963) was the first who postulated the existence of such-type relationships and proposed to name them the "generalized reciprocity relationships". It is simple to show that the Onsager's symmetry conditions ensue directly from these differential relationships for a particular case of linear systems. In fact, applying (Eq. 10-2) one can obtain:

$$(\partial J_i /\partial X_j) = L_{ij} = (\partial J_j /\partial X_i) = L_{ji} \qquad (11)$$

Thus, the famous Onsager's reciprocal relations ensue as a corollary of more general differential relationships of thermodynamics and do not need involving whatever statistic-mechanical considerations. However, utility of these parities is not settled at all by a possibility to replace with them the Onsager's symmetry conditions. Becomes obvious that the generalized (differential) reciprocal relations do not depend on a type of phenomenological laws. It gives to them the status of conditions of involved "from the outside" for short circuit of system of its equations (similarly to the equations of a condition in thermodynamics). In that case limitation or an inaccuracy of these equations concerns not bases of the theory and only its consequences depending from them. This independence of reciprocal relations (Eq. 10) from a hypothesis of local equilibrium and a principle of linearity allows to distribute OIP to the nonlinear systems making useful work (Etkin, 2010).

The specific form of such equations is established, naturally, by experiment. Linear phenomenological Onsager's laws with constant coefficients L_{ij} represent only their special case. The majority of actual processes of transfer (thermal conductivity, electric conductivity, diffusion and viscous friction, described by Fourier's, Ohm's, Fick's and Newton's laws, etc., are quasi-linear as a phenomenological coefficients L_{ij} in them depend on temperature and other parameters of a condition.

It is essentially important in this respect that parities (Eq. 10) are satisfied and in that case when in Eq. 2 are constant only "non-diagonal" coefficients L_{ij} $(i \neq j)$. It essentially expands area of applicability of Onsager's symmetry conditions and explains, why they are justified far outside fairness of those assumptions which have been laid in the basis of their statistic-mechanical background. Very important that at $L_{ij} \neq$ const from (Eq. 10) can receive so-called "additional" parities of reciprocity between diagonal L_{ii} and non-diagonal L_{ij} phenomenological coefficients (Gyarmati, 1960):

$$(\partial L_{ii} /\partial X_j) = (\partial L_{ij} /\partial X_i), (i \neq j) \qquad (12)$$

Moreover, reciprocity relations (Eq. 10) appear fair as it will be shown below and in that case when composed the right part (Eq. 2) have a different sign that is characteristic for processes of transformation of energy and leads to Cazimir's parities, instead of Onsager's symmetry conditions.

Finally, parities of reciprocity (Eq. 10) appear fair and for essentially nonlinear systems with exponential kinetic laws as well as for systems for which these laws at all have no the matrix form Eq. 2. All this does parities (Eq. 10) reliable tool in hands of researchers, allowing

them not only to reduce number of coefficients L_{ij} as a subject of experimental definition but also to make sure in a correctness of the used equations of transfer and the physical models put in their basis.

Anti-symmetry of reciprocal relations for processes of inter-conversion of energy: Let's consider any power installation in which ith form of energy will be transformed to jth. It means, that brought to it (initial) and allocated from it (transformed) capacity have a various sign ($N_i = X_i.J_i < 0$; $N_j = Xj.J_j > 0$). In that case the kinetic equations of processes the relaxations (Eq. 2) postulated by L. Onsager, make room for phenomenological laws of a type (Etkin, 2010):

$$J_i = L_{ii} X_i - L_{ij} X_j \qquad (13)$$

$$J_j = L_{ji} X_i - L_{jj} X_j \qquad (14)$$

Such character of laws of transformation of energy well is illustrated on an example of the transformer in which a flow of primary energy carrier J_i (the electric current on an input in its primary winding) will be transformed in the beginning to a magnetic flow in its core and then restores the form in a secondary winding with other number of coils and other parameters. Thus, as is known, current J_i decreases when force X_j increases and becomes minimal in so-called "no-load" operation", when ($J_j = 0$). On the contrary, J_i increases, when X_j decreases (with approximation to "a mode of short circuit", where $X_j = 0$). In the similar image a flow J_j (for example, the current in a secondary winding of the transformer) increases with increase of a pressure on primary winding X_i and with a power failure on secondary winding X_j.

If non-diagonal coefficients of proportionality L_{ij} and L_{ji} in these equations are constant, application to them of differential parities of reciprocity (Eq. 10) leads to the conditions of anti-symmetry (Casimir, 1945):

$$(\partial J_i / \partial X_j) = -L_{ij} = (\partial J_j / \partial X_i) = L_{ji} \qquad (15)$$

This circumstance throws fresh light on the origin of the Cazimir's reciprocity relationships $L_{ij} = L_{ji}$ exposing the underneath meaning of the requirements for different parity of forces with respect to time inversion. In fact, for the dissipation forces not changing their signs with time inversion (i.e., for the so-called "α-type forces") the Onsager's symmetry conditions $L_{ij} = L_{ji}$ as shown above, are valid. Whenever a part of these forces have the reversible character (i.e., refer to the "β-type forces"), the Onsager's reciprocity relationships give place to anti-symmetry conditions $L_{ij} = -L_{ji}$. At the same time the

consideration endeavored here shows that the applicability of the Cazimir's relationships is not actually restricted to the different-parity forces (α and β-type) case. In fact, let us assume dealing with energy conversion processes of purely dissipative character. Such are in particular, thermal conductivity, electric conductivity, diffusion and viscous friction described by Fourier's, Ohm's, Fick's and Newton's laws and resulting in only the substance and energy transfer. In this case all terms of kinetic Eq. 2 describing vector phenomena have the same sign $X_i.J_i > 0$ defined by their contribution to dissipative function TdS/dt. In this case reciprocity relationships (Eq. 11) defining value and sign of the phenomenological coefficients L_{ij} in linear kinetic Eq. 2 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 ith form of energy into the jth one in various machines apply to these effects, too. This substantially extends the applicability of the anti-symmetrical reciprocal relations (Etkin, 1989).

Confirming of anti-symmetric reciprocal relations: It is a matter of interest to confirm the anti-symmetrical reciprocity relationships (Eq. 4) in reversible processes on a wide class of the processes, submitting to the Maxwell's equations (Rysselberghe, 1963). For this purpose we shall consider process of inter-conversion electric (index "e") and magnetic (index "m") energy in system of type of already mentioned transformer. If to neglect losses in this process, the right part of identity (Eq. 5) will address in zero. Representing for convenience members of its 2nd sum through parameters of spatial heterogeneity X_e, Z_e and X_M, Z_M in their scalar form in view of a sign on work we shall find:

$$d \ni_V = X_e dZ_e - X_M dZ_M = 0 \qquad (16)$$

Thus, differential parities of reciprocity (Eq. 10) will become:

$$(\partial X_e / \partial Z_M) = -(\partial X_M / \partial Z_e) \qquad (17)$$

Let us consider a system consisting of a closed electric circuit with an arbitrary length ℓ_e and variable (in general case) cross section f_e which comprises an as well closed magnetic circuit with a length ℓ_m and cross section f_m variable thru the length. In this case in the Eq. 14 X_i and X_j represent accordingly electromotive $X_e = \int E.d \; \ell_e$ and magneto-motive $X_M = \int E.d \; \ell_e$ forces (Rysselberghe, 1963) while $J_e = \int (dD/dt)df_e$; $J_M = \int (dB/dt)df_M$ total fluxes of electric and magnetic displacements, respectively, sometimes named the "linkage fluxes" and traditionally represented by the number of the lines of force linking the cross section of the electric and magnetic circuits, respectively. Here, E, H electric and magnetic fields; D, B vectors of electric and magnetic induction.

Let us now change based on the Stokes theorem, in the force equation $X_e = \int E.d \; \ell_e$ from the curvilinear integral taken over the closed electric circuit with a length of ℓ_e to the integral $\int rotE.df_M$ over the magnetic circuit cross section f_M. In the similar way one can change in the force equation $X_M = \int H.d\ell_M$ from the curvilinear integral over the closed magnetic circuit with a length of ℓ_M to the integral $\int rotH.df_e$ over the surface f_e covering the electric circuit. Then $\partial X_e / \partial f_M = rotH$; $\partial X_M / \partial f_e = rotH$; $\partial^2 Z_e / \partial f_e \partial t$ $\partial J_e / \partial f_e = dD/dt$ and $\partial^2 Z_M / \partial f_M \partial t = \partial J_M / \partial f_e = dB/dt$. Substituting these expressions in reciprocity relations (Eq. 11), we shall find:

$$rotE = -dB/dt \qquad (18)$$

$$rotH = dD/dt \qquad (19)$$

These equations differ from the corresponding Maxwell's equations in that they contain the total time derivatives of electric and magnetic induction vectors. This is not a surprise since the primary equations of thermodynamics (Eq. 4) contain the exact differentials of vectors r_i. To form Eq. 15 and 16 into a more habitual type, we shall consider that $dD/dt = j_e + (\partial D / \partial t)$ where $j_e = \varrho_e v = (v.\nabla)D$-conduction current caused by the free charge transfer whereas magnetic analogs to the free charge ρ_e do not exist ($\nabla B = 0$) and $d \; B/dt = (\partial B/\partial t)$. Reception of Maxwell's equations as consequences of anti-symmetric parities of reciprocity confirms fairness of these of a parity and for an extensive class of the processes, submitting to the mentioned equations.

Applicability of differential reciprocal relations to non-linear systems: To make sure in fairness of differential parities of reciprocity (Eq. 10) to the interconnected chemical reactions, consider for example the case of interrelated chemical reactions obeying the Guldberg and Waage chemical kinetics laws). For this let us apply to the class of ternary uni-molecular reactions Onsager earlier considered. These reactions with substances L, M, N may be described by scheme:

$$L \leftrightarrow M \; (reaction \; 1); \; M \leftrightarrow N \; (reaction \; 2);$$
$$N \leftrightarrow L \, (reaction \; 3) \qquad (20)$$
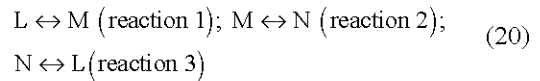
This scheme describes a reaction mechanism, i.e., a real chemical conversion process (Haase, 1969). The above elementary reactions run with rates w_{1-3}, respectively, being expressed, according to the Guldberg and Waage laws, by the following exponential kinetic equations:

$$w_1 = \omega_1 '[1 - \exp(-A_1/R_m T)] \qquad (21)$$

$$w_2 = \omega_2 '[1 - \exp(-A_2/R_m T)] \qquad (22)$$

$$w_3 = \omega_3 '[1 - \exp(-A_3/R_m T)] \qquad (23)$$

Where:
ω_{1-3}' = Rates of the corresponding direct reactions
A_{1-3} = Their current affinities
R_μ = Universal gas constant

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 and Mazur, 1962). Therefore, let us introduce two new linear-independent rates:

$$w_a = w_1 + w_2; \; w_b = w_2 + w_3 \qquad (24)$$

Two independent forces A_α and A_β correspond to these rates which allows Eq. 21-23 to be transformed, subject to the invariance of the dissipation function TdS/dt to the matrix form:

$$w_a = L_{11}[1 - \exp(-A_a/R_m T)] + L_{12}[1 - \exp(-A_b/R_m T)] \qquad (25)$$

$$L_{11} = \omega_1 ' + \omega_2 '; \; L_{12} = \omega_3 ' \exp(-A\alpha/R_m T)] \; ;$$
$$L_{21} = \omega_3 ' \exp(-A_\beta/R_m T)]; \; L_{22} = \omega_1 ' + \omega_3 ' \qquad (26)$$

Here:

$$L_{11} = \omega_1 ' + \omega_2 '; \; L_{12} = \omega_3 ' \exp(-A_\alpha/R_m T)];$$
$$L_{21} = \omega_3 ' \exp(-A_\beta/R_m T)]; \; L_{22} = \omega_1 ' + \omega'_3 \qquad (27)$$

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_{1-3}' being functions of temperature, pressure and concentrations of parent substances for the corresponding reaction do not depend on its affinity. In fact, the affinity A_r of any of the rth 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 (Eq. 9) should be true having in our case the form:

$$\partial w_\alpha / \partial A_\beta = \partial w_\beta / \partial A_\alpha \qquad (28)$$

To make sure they are valid, it is enough to differentiate expression (Eq. 25) with respect to A_β, given L_{11} and L_{12} independent on A_β and to repeat the similar operation on Eq. 26 with respect to w_β. The result will be as follows:

$$\partial w_a / \partial A_b = \partial w_b / \partial A_a = (\omega_3' / R_m T) \exp(-A_3 / R_m T) \qquad (29)$$

It can be easily seen that with approaching equilibrium, when A_{1-2} are simultaneously tending to zero, relationship (Eq. 29) goes over into known Onsager's symmetry conditions for chemical reactions in the form:

$$L_{12} = L_{21} = \omega_3' / R_m T \qquad (30)$$

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. It opens up additional vistas in the thermodynamic analysis of chemical technology processes and the evolutional problems of biological and ecological systems.

The further reduction of number of phenomenological coefficients: Let's assume, that the processes proceeding in investigated system are independent or that we consider only one process J_i in it, for example, electric current J_i or diffusion of kth substance J_k each of which arises as is known, under action of several making F_{ij} residual force F_e or F_k. In that case differential parities of reciprocity in Eq. 7 and 8 $(\partial F_i / \partial v_j) = 0$ and $(\partial F_j / \partial v_i) = 0$ as

they reflect interrelation of processes. The reference in zero of differential parities of reciprocity means that the generalized speed of any ith independent process v_i cannot depend on "Foreign" force F_{sj} so, phenomenological laws of carry assume air this case more simple:

$$J_i = L_i F_i = L_i \Sigma_j F_{ij} = L_i \Sigma_j \Theta_j X_j \qquad (31)$$

where, L_i the factor describing conductivity of system. These laws are fair and in that case when flows J_i and J_j are independent. It does not contradict the Onsager's postulate, according to which speed of any relaxation process v_i (named by it flow J_i) depends on all motive forces X_j operating in system. Such (diagonal) form of the kinetic equations of transfer conform to laws conform to laws Fourier, Ohms, Fick, Darcy and Newton in which the unique motive force is replaced on resulting of all forces X_j operating in system.

However, in that case differential parities of reciprocity in the Eq. 7 and 8 make room for the similar parities connecting among themselves stream J_k or J_e with components F_{ij} unique (resultant) of force $F_i = \Sigma_j F_{ij} = \Sigma_j \Theta_j X_j$. Really, expression (Eq. 31) defines flow J as function of thermodynamic forces X_j, allowing to consider t hermodynamic parameters Θ_j as private derivatives $(\partial J_i / \partial X_j)$. Thus, we also come to differential parities (Eq. 10) that nonfirms fairness of phenomenological laws (Eq. 31). According to these laws, flows J_i disappears at the reference in zero of resulting forces F_i, i.e., with the reference in zero of the sum $\Sigma_j \Theta_j X_j$. It leads to occurrence of communications between components $F_{ij} = \Theta_j X_j$ resulting forces F_i which are however, consequence of imposing not streams J_i, J_j and forces X_i, X_j (that will quite be coordinated with mechanics and electrodynamics). Such "superposition effects" especially, simply to find, if in system any two thermodynamic forces $X_i = -\nabla_{\psi i}$ and $X_j = \nabla_{\psi j}$ operate. Then, $\Theta_i X_i + \Theta_j X_j = 0$ and between forces X_i and X_j there is the parity on the outside reminding expression so-called "stationary superposition effects":

$$(N\psi_j / N\psi_i) = -\Theta_i / \Theta_j) \qquad (32)$$

However, now in the right part (Eq. 32) there are no kinetic factors of type L_{ij} which appeared in expressions of stationary effects in TIP (Haase, 1969):

$$(N\psi_j / N\psi_i)_{CT} = -L_{ij} / L_{jj} \qquad (33)$$

Therefore, than them would be more proper to name conditions of "partial equilibrium of ith sort" to similar

conditions of thermal, mechanical and material equilibrium in classical thermodynamics. Such situations when in system one behind another processes proceeding in it stop all are peculiar to all poly-variant systems. It sheds new light an origin of numerous stationary effects in TIP which maintenance of "order" due to external compulsion and "entropy productions" now speak (Maxwell, 1881). Expression (Eq. 34) allows on known parameters Θ_i and Θ_j to predict not only character but also size of these effects or on the contrary on their size to find a number parameters of a condition not giving in to measurement.

As an example of simplification of transport laws we shall consider the equations of multi-component isobaric-isothermal diffusion for which Onsager (1931) proposed the phenomenological laws of the kind:

$$J_i = -\Sigma_j L_{ij} \nabla \mu_j, \ (i, j = 1, 2, \dots, K-1) \qquad (33)$$

Unlike (Eq. 32) this equation assumes that the flow J_i 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 jth components μ_j. The additional (non-diagonal) terms $i \neq j$ of the first sum of this expression were introduced by 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 jth substances is a function of temperature T, pressure p and concentration c_k of the independent kth components its differential $d\mu_j$ at p, T = const features exclusively its dependence on concentration which may be expressed as:

$$d\mu_j = \Sigma_k (\partial \mu_j / \partial c_k) dc_k = \Sigma_k \mu_{jk} dc_k \qquad (35)$$

where, μ_{jk} is abrtuidged symbol for the derivative $\partial \mu_j / \partial c_k$. Therefore, Eq. 34 contains a double sum of factors of proportionality at concentration c_k. At existing methods of experimental definition of fields of concentration of impurity in metals and alloys it does practically the important problem of a finding of not diagonal factors of multi-component diffusion in them not simply extremely complex but also mathematic incorrect (Etkin, 1998).

In the mean time the same problem rather simply is solved at record of the law of diffusion in Eq. 34 when number F_{ij} includes a number of forces of concentration diffusion $X_k = -\nabla c_k$ and the role of parameters X_j is carried

out with derivatives $\mu_{kl} \equiv (\partial \mu_k / \partial c_l)$. In that case laws of multi-component concentration diffusion assume air more simple:

$$J_i = -\Sigma_l D_{kl} X_l (i, k, l = 1, 2, \dots, K-1) \qquad (36)$$

Here, $D_{kl} = L_i \mu_{kl}$ 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 coefficients of diffusion D_{kl} and thermodynamic factors of diffusion μ_{kl}:

$$D_{kl} / \mu_{kl} = D_{ki} / \mu_{ki} \qquad (37)$$

The relationship of such a kind was set up earlier by of some assumptions by Brown and Kirkaldy (Etkin, 1993). Owing to such expression of superposition effects through thermodynamic variables we have the possibility to predict an opportunity on known parameters Θ_i and Θ_j not only character but also size of these effects or on the contrary on their size to find a number of parameters of the condition not giving in to measurement (Etkin, 1998).

However, the most important value of the parities received here besides their generality consists first of all that they allow to carry out the further reduction of number of the kinetic factors L_{ij} which is a subject experimental definition from n (n+1)/2 (in TIP) up to n. Especially effectively such reduction for processes of anisotropic heat conductivity and electric conductivity in a magnetic field where all entire spectrum of the thermo-resistive, thermo-electric, thermo-magnetic and galvano-magnetic effects in the longitudinal and transverse magnetic fields may be expressed using only 4 phenomenological coefficients. It is reached due to an establishment of additional parities between the specified effects. From five additional parities received at it the most meaningful is the parity between effects of Righi-Leduc and Hall, known earlier from the electronic theory of metals as well as a parity between effects of Righi-Leduc and Ettinshausen-Nernst, known as Wiedemann-Franz law (Etkin, 2010). That these parities get the status of consequences of thermodynamics.

Except for that, the differential relationships between the state parameters and their functions enable solution of also other problems. In particular, they allow to count fundamental functions of a condition of system of type of its energy on experimental data to find restrictions with which should satisfy physical models of system or process to exclude cases missing or

superfluous number of variables of a condition, etc. In particular, they allow calculating by experimental data the fundamental state functions of a system, 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.

CONCLUSION

Unlike existing TIP, based a hypothesis of local equilibrium, expansion of classical thermodynamics on non-static processes of transfer expediently to begin with generalization of its basic equation on spatially non-uniform systems with introduction in it of concepts of time, speed and motive powers of actual processes.

Introduction of parameters of spatial heterogeneity of investigated systems Z_i and X_i allows to distribute a thermodynamic investigative method of the phenomena of transfer to processes of useful transformation of various forms of energy.

Refusal of allocation of an irreversible part of actual processes and a finding of streams J_i and forces X_i on more general basis, than "entropy production", releases from an indispensability of preparation of the bulky "balance equations" of weight, a charge, an impulse, energy and entropy investigated non-equilibrium systems.

Mathematical properties of full differential of non-equilibrium parameters allow to give consistently thermodynamic background of differential reciprocal relations, more general, rather than a Onsager's symmetry condition or a Cazimir's anti-symmetry condition.

Onsager's and Cazimir's reciprocal relations result from the mentioned parities in specific case the linear systems, submitting to submitting to linear phenomenological laws with constant phenomenological coefficients L_{ij}.

The specified parities of reciprocity remain fair and in that case when only not diagonal factors in its matrix phenomenological laws are constant. It explains, why they are justified and outside those restrictions which were imposed by their statistic-mechanical background.

Differential reciprocal relations applicable to processes of useful transformation of energy that proves to be true by a conclusion to their basis of Maxwell's equations to which the wide class of converters of energy submits.

These reciprocal relations are fair and for essentially nonlinear systems that is proved on an example of the threefold chemical reactions submitting to exponential laws. Thus, differential reciprocal relations pass in Onsager's symmetry conditions in process of approximation of system to equilibrium.

Application of differential reciprocal relations allows to simplify phenomenological laws of trabsfer by a finding resulting of thermodynamic forces X_i operating in system. Use of differential reciprocal relations for giving to transport laws of the diagonal form allows to find numerous "superposition effects" diverse processes as result of the mutual compensation of making F_{ij} without use of kinetic coefficients L_i or L_{ij} a subject experimental definition.

Varied of the "stationary effects" can be expressed extremely through thermodynamic variables, getting in this case sense of conditions of partial (current) equilibrium. These conditions reflect alternate disappearance of flows J_i in process of approximation of system to equilibrium and consequently are fair and for non-stationary conditions.

This method allows to find additional communications between kinetic coefficients L_{ij} and by that to carry out the further reduction of their number from n (n+1)/2 in OIP up to n. Fairness of this position is confirmed on examples of multi-component diffusion and the phenomena of anisotropic heat-and electric conductivity in metals.

The adequate description of a condition of non-equilibrium systems in view of their spatial heterogeneity allows to give reciprocal relations a strict thermodynamic background that essentially expands area of their applicability.

REFERENCES

Bejan, A., 2016. Advanced Engineering Thermodynamics. 4th Edn., John Wiley & Sons, Hoboken, New Jersey, ISBN:978-111-928-10-30, Pages: 751.

Casimir, H.B.G., 1945. On onsager's principle of microscopic reversibility. Rev. Mod. Phys., 17: 343-347.

De Groot, S.R. and R. Mazur, 1962. Non-Equilibrium Thermodynamics. Elsevier, Amsterdam, Netherlands,.

Denbigh, K.G., 1951. Thermodynamics of the Steady State. Methuen Publishing, New York, USA., Pages: 103.

Etkin, V.A., 1988. The fundamental equation of non-equilibrium ther-modynamics. Russ. J. Phys. Chem., 62: 1157-1159.

Etkin, V.A., 1989. Origin of Onsager's reciprocal relations. Soviet. J. Appl. Phys., 4: 288-293.

Etkin, V.A., 1993. Reciprocal relations of reversible processes. Soviet. J. Appl. Phys., 1: 62-64.

Etkin, V.A., 1998. Synthesis and new applications of the energy transfer and energy conversion theories. Ph.D Thesis, Bauman Moscow State Technical University, Moscow, Russia.

Etkin, V.A., 2010. Thermokinetics: Synthesis of Heat Engineering Theoretical Grounds. Lulu.Com, Morrisville, North Carolina, ISBN:978-0-557-25040-0, Pages: 334.

Fitts, D.D., 1962. Nonequilibrium Thermodinamics. McGraw-Hill Education, New York, USA., Pages: 168.

Groot, S.R.D. and P. Mazur, 2013. Non-Equilibrium Thermodynamics. Dover Publications, New York, USA., Pages: 516.

Groot, S.R.D., 1951. Thermodynamics of Irreversible Processes. Elsevier, Amsterdam, Netherlands, Pages: 242.

Gyarmati, I., 1960. Introduction to irreversible thermodynamics. Medical Training Initiative (MTI), Budapest, Hungary.

Haase, R., 1969. Thermodynamics of Irreversible Processes. Addison-Wesley, Darmstadt, Germany,.

Kondepudi, D. and I. Prigogine, 2014. Modern Thermodynamics: From Heat Engines to Dissipative Structures. 2nd Edn., John Wiley & Sons, Hoboken, New Jersey, USA., ISBN:978-1-118-37181-7, Pages: 186.

Maxwell, J.C., 1881. A Treatise on Electricity and Magnetism. 2nd Edn., Oxford University Press, Oxford, England, UK.,.

Meixner, I., 1954. [Thermodynamics of Irreversible Processes]. Aachen Publisher, Aachen, Germany, Pages: 178 (In Germany).

Ness, H.C.V., 2015. Classical Thermodynamics of Non-Electrolyte Solutions. Elsevier, Amsterdam, Netherlands, ISBN:9781483225470, Pages: 174.

Onsager, L., 1931. Reciprocal relations in irreversible processes. II. Phys. Rev., 37: 405-426.

Prigogine, I., 1947. [Thermodynamic Study of Irreversible Phenomenes]. Dunod Publisher, Liege, Belgium, Pages: 143 (In French).

Rysselberghe, P.V., 1963. Thermodynamics of Irreversible Processes. Blaisdell Publishing Company, Waltham, Massachusetts, Pages: 165.

Sandler, S.I., 2017. Chemical, Biochemical and Engineering Thermodynamics. 5th Edn., John Wiley & Sons, Hoboken, New Jersey, USA., ISBN:978-0-470-50479-6, Pages: 1007.