Part 4

THERMODYNAMIC ANALISYS OF PHENOMENA AT SCIENTIFIC DISCIPLINES INTERFACES

To solve problems arising at the boundary interfaces between fundamental disciplines, a theory is quite necessary allowing a unified description for physical, chemical, biological and the like properties and forms of the material world. Hereafter a thermodynamic theory of such a type will be brought forward as applicable to transfer processes regardlesss of the field of knowledge they belong to. This theory will not only expose the unity of regularities in progressing transfer processes pertaining to various scientific disciplines. It will provide an absolutely other interpretation for origin of multiple thermomechanical, thermodiffusional, thermoelectrical, thermomagnetic, electromechanical, thermogalvanomagnetic, etc effects appearing at simultaneous progress of dissimilar processes. It will be shown that these effects are caused not by synergism (mutual intensification) of irreversible processes as commonly accepted, but, on the contrary, by their counterdirectivity and the associated partial reversibility. Thereby one more step will be made on the way toward the unified theory of energy conversion in any forms, which is the primary content of energodynamics.

This theory will have also a pronounced applied character owing to the wide application of the mentioned effects in modern manufacturing processes.

Chapter 15.

FUNDAMENTAL UNITY OF ENERGY TRANSFER PROCESSES

A great number of disciplines study energy transfer processes in solid, liquid and gaseous media, plasma and electromagnetic fields: physical and chemical kinetics, the theory of irreversible processes and continuum mechanics, statistical physics and acoustics, optics and hydrodynamics, electrodynamics and magnitohydrodynamics, high-energy physics, etc. Each of these disciplines has its own methodological features, notional system and specific body of mathematics. In this context it is a matter of great significance to reveal the fundamental unity in description of these processes and to ascertain the basic regularlities of their kinetics. These are the problems that predetermine the contents of this chapter.

15.1. Wave-Forms-of-Energy Transfer Processes

In modern physics matter is subdivided into substance and field. Substance means a set of discrete formations having a rest mass (atoms, molecules, etc), whereas force field (gravitational, electromagnetic) means a continuum having zero rest mass. However, from the positons of the quantum theory this difference practically disappears: field loses its continual character with introducing quantums – photons and gravitons, while the matter particles – protons, neutrons, electrons, mesons – lose their discrete properties and become quantums of the corresponding fields (nucleon, mesonic, etc) featuring rest mass. The most widespread theory of elementary particles called "Standard Model" assumes specific particles – interaction carriers – spreading in void space with a constant (limit) velocity and existing for each kind of interaction. These particles do not have rest mass and move with a constant velocity omitting the acceleration and deceleration stage. Therefore the concepts and laws of mechanics are inapplicable to them. No wonder thus that such a theory is able to satisfactorily explain neither the origin of particles – interaction carriers – and their variety, nor the 'wave-particle' dualism, nor the fact of proton simultaneously passing through two holes and its self-diffraction. Moreover, the explanation in the Standard Model that the interaction is an irradiation and absorption by matter particles of some other particles means the latter have been a part of the composition, which makes the process of searching for "elementary" (fundamental) particles never-ending, as a matter of fact. In short, such corpuscular theories raise more problems than solve.

These shortcomings are not intrinsic to the wave theories assuming some medium of wave propagation – either solid, liquid, gaseous bodies, or electromagnetic field that is construed now as a specific kind of matter, or ether that, on the contrary, is not so far considered as matter[1].

Meanwhile, ether should have been long considered as an indispensable component of any material system. N. Tesla's experiments are one of the weighty argument in favor of such a standpoint . In his attempts to reproduce in 1889 the Hertz's experiments (1987) he discovered a radiation of absolutly specific kind. The radiation that he called "radiant" appeared in the secondary winding turns of his transformer that tranformed high-voltage discharge rates. It came from the copper wire surface and spread as a gaslike shining cloud that, however, could not be photographed. That radiation had a terrific permeability – even metal screens impermeable for electromagnetic waves were not a barrier for it. At a pulse duration above 100 μsec those waves exerted a painful "shock" influence on the human organism with no protection against. Those waves generated a spatially distributed voltage that was thousands times as high as the initial voltage on spark discharger and amounted to many millions of volts. That radiation generated a charge equivalent to a very high current on the metal object that were on its way. That radiation easily penetrated through degasified devices and caused a bright glow of burned-out bulbs. In a row of in-series lamps copper bus-bridged the "radiant" energy flux chose the max-resitance path, whereas usual electric current passed through the bus. Based on those and other distinguishing features, N. Tesla came to a conclusion that the radiations he discovered were "waves in ether like radio waves and light".

While the Maxwell theory lead to an idea that the electromagnetic waves were a series of electrical disturbances (quite low electric currents) that became consequently exited in ether, the N. Tesla's experiments resulted in something other since ether is electrically neutral. That meant that ether as itself did not have electromagnetic properties – such oscillations appear in the Hertz vibrator (antenna) and then transform into ether vibrations. These are the vibrations ether transfers to the resonator – a detector wherein they are transformed into electromagnetic oscillations again. Hence it followed that ether was an a mediator transporting the en-

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[1] Despite the fact that A. Einstein himself, who "ousted" the ether from theoretical physics when created the special reletivity theory in 1905, had to ackoowldge as soon as in 1924: "In theoretical physics we cannot do without the ether as a continuum provided with physical properties" // A. Einstein "About ether", 1924, Transactions, M., Nauka, 1966, v. 2, p. 160.

ergy of electromagnetic oscillations ocurred in a substance within any frequency spectrum, i.e. vibrations of another nature.

As a staunch supporter of such a non-electromagnetic nature of the radiant waves, N. Tesla in 1889 visited H. Hertz and made an attempt to pursuade him in the fallaciousness to interpret the oscillations the latter had discovered in space as electromagnetic ones. However, this fact has usually been hushed up in the history of science and in teaching literature.

Meanwhile, many enough factors have been accumulated to date evidencing the existence of a non-electromagnetic radiation. At least a dozen names given to this radiation by various investigators are known today. Recollect just some facts. Yet in 1906 the professor N. P. Myshkin reported an absolutely inexplicable behavior of a thin mica disc suspended on a finer thread inside a copper vessel heat insulated and screened with a light-tight paper. The disc twisted the thread in response to the candle light, displacement of people and inanimate objects relative to the disc and sometimes with no obvious reason at all.

In forties-fifties of the last century the doctor Reich, a Freud's collegue, elaborated a number of physical devices to detect and log an unknown nature he called the "orgonom".

In 1948 the astrophysicist N. Kozyrev discovered a specific kind of radiation exisiting and penetrating through the telescope objective lens shuttered with a metal blind. Those experiments were then repeated by other investigators who confirmed the superphotonic propagation velocity of those radiations. A component of a non-electromagnetic nature have recently been discovered in the radiation from the small-capacity optical quantum generator (V.V. Kvartalnov, N.F. Perevozchikov, 1999).

There are two more facts evidencing the different nature of oscillations in the Hertz vibrator and in ether. As Maxwell repeatedly stressed, his theory was based on the concept of interconversion between energies of electric and magnetic fields. The same follows from the thermodynamic derivation of Maxwell's equations (8.2.15) – (8.2.16) in Chapter 8 from the law of their sum conservation. However, from the Maxwell's equations derived it follows that in electromagnetic waves radiated the magnetic wave antinode corresponds to the electric wave antinode (in-phase waves), which leads to an obvious violation of the law of electromagnetic energy conservation in free space. This contradiction can be removed by acknowledging the fact that the electric and magnetic components of electromagnetic wave have different power and by including into the energy balance a third component – ether wave. The validity of such an assumption is confirmed by the fact that no a least perceptible magnetic component available in space has been experimentally proved so far.

We have considered the above in order to show the possibility of energy transfer in space by ether waves not resorting to model representations of their physical nature (hydro-acoustic, electromagnetic, gravitational, etc) and considering them to be independent of the nature of oscillations in their source. This opens a direct way to the unified theory of field since the travelling waves the in any medium may be interpreted as periodical disturbances of this medium spreading therein with a certain velocity depending on only the medium properties. In this respect especially attractive are the wave theories based on the model of solitons – solitary waves featuring corpuscular properties (see Chapter 9). Such theories eliminate the wave-particle dualism problem and allow a unified description of transfer processes in substance and field using such conventional parameters of material media as density, coefficient of elasticity, velocity of disturbance propagation, etc. These parameters allow finding kinetic and potential energies of travelling wave of any nature (hydro-acoustic, electromagnetic, ether) by representing their sum E_B in the unified form of (9.1.6). Then a possibility appears to introduce the notion of force causing the energy transfer in these media, to explain the transfer velocity variation with changing from meduim to medium, to find the conditions of disturbing equilibrium between field and substance and to quantitatively describe the energy exchange between them.

To show that the energy transfer by any type of waves obeys the same transfer kinetic equations as for the substance forms of energy, use the general expression for their energy densities (9.1.6). The total variation of the energy $E_B(\mathbf{r}, t)$ with time is known to include, besides the local derivative $(\partial E_B/\partial t)$, also the component $(\mathbf{v}_B\nabla)E_B$ caused by the energy transfer in space. According to energodynamics this component may be represented as the product of the energy carrier flux $\mathbf{J}_B$ and the thermodynamic force $\mathbf{X}_B$ causing it. According to (9.1.8)

$$d_{\mathrm{r}}\mathbf{E}_B/dt \equiv (\mathbf{v}_B\cdot\nabla)E_B = A_B\nu\mathbf{v}_B\nabla(A_B\nu) = -\,\mathbf{J}_B\cdot\mathbf{X}_B\,, \qquad (15.1.1)$$

where $\psi_B = A_B\nu$ – wave potential that could reasonably be called *amplitude-frequency*; $\rho\mathbf{J}_B = \rho\psi_B\mathbf{v}_B$ – soliton flux density (Chapter 9); $\mathbf{v}_B$ – velocity of solitons; $\mathbf{X}_B = -\,\nabla(A_B\nu) = -\,\nabla\psi_B$.

This expression is identical to (8.5.4) for electrical and magnetic fields $\mathbf{E}\cdot\mathbf{j}_e{}^c$ and $\mathbf{H}\cdot\mathbf{j}_M{}^c$, where the motive forces $\mathbf{X}_e$ and $\mathbf{X}_M$ are construed as electric and magnetic intensities **E** and **H,** respectively.

As earlier noted, the displacement fluxes differ from the material energy carriers considered in the theory of irreversible processes because they do not cross the system borders together with the energy flux, i.e. are internal ones. In other respects they show up as similar to the material fluxes, i.e. are the energy carrier redistribution process causing the system energy ordering.

Thus the fluxes of field and matter energy forms feature the unified interpretation in energodynamics. This unity is not just formal (descriptive), but bears a deep physical nature. In particular, the wave field can also exert force influence like the gravitational and electrostatic fields. To expose the nature of the wave force influence, let us take into account that any wave is a bilateral deviation of some varying value from its equilibrium, i.e. generates the spatial heterogeneity of the medium wherein it is propagating. To find the distribution moment $\mathbf{Z}_w$ describing this heterogeneity, let us select from an arbitrary wave sequence a part with the monotonous increase or decrease of the varying values (in our case the density ρ_w of the parameter Θ_w (Fig. 15.1)).

The crosshatched regions in this figure describe the Θ_w value "deficiency" forming as a result of the Θ_w transfer in oscillating process from one space region to another. As a result the centers of the values Θ_w' and Θ_w'' equal to the crosshatched regions are displaced from the positions $\mathbf{r}_o'$ and $\mathbf{r}_o''$ they would occupy at a uniform distribution of ρ_w for a quarter of period to positions $\mathbf{r}'$ and $\mathbf{r}''$. The distribution moment $\mathbf{Z}_w$ in this case will be descrided by the expression (1.5.6) wherein the elements $d\Theta_i$ are replaced by Θ_w^*:

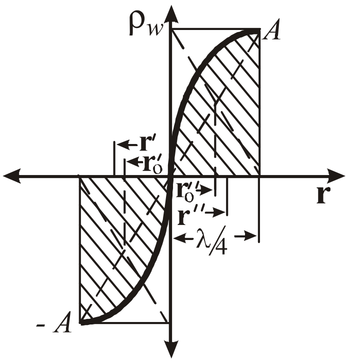

Fig. 15.1. To formation of distribution moment in single wave

$$\mathbf{Z}_w = \mathbf{r}'\Theta_w' + \mathbf{r}''\Theta_w''. \qquad (15.1.2)$$

It is significant that the summands (15.1.2) are not compensated, but summarized since the signs of Θ_w' and Θ_w'', as well as of the displacements $(\mathbf{r}' - \mathbf{r}'_o)$ and $(\mathbf{r}'' - \mathbf{r}''_o)$ are opposite. This allows representing (15.1.2) in the same form as the dipole moment:

$$\mathbf{Z}_w = \Theta_w^* \Delta\mathbf{r} \,, \qquad (15.1.3)$$

where $\Delta\mathbf{r} = \mathbf{r}'' - \mathbf{r}'$ – analog of the electric or magnetic dipole arm. This allows finding the motive force for the wave form of energy exchange in the same way as for the polarization processes, i.e. as the derivative of the wave energy U_w with respect to the distribution moment $\mathbf{X}_w = -(\partial U_w/\partial \mathbf{Z}_w)$. Thus should oscillations arise in some medium, it appears to be locally polarized. The scale of the spatial heterogeneity thus generated can be several orders lower than for the long-range gravitational and electromagnetic forces, therefore the resultant $\mathbf{X}_w$ for macrosystems as a whole may appear to be zero. However, for microsystems (i.e. at atomic and subatomic levels) such a heterogeneity can play a decisive role in the energy exchange between field and matter.

It is significat to note one feature of the wave force influence associated with the steepness of wave edge. For this let us express the wave amplitude $A_{\text{В}}$ in terms of the wave length λ by introducing the wave form factor $k_{\text{В}}$ through the relation:

$$k_{\text{В}} = A_{\text{В}}/4\lambda \, . \tag{15.1.4}$$

The possibility of such a relation $A_{\text{В}} = A_{\text{В}}(\lambda)$ becomes especially evident when representing the half-wave profile in Fig. 15.1 as an equivalent pulse of the triangle form with a height of $2A_{\text{В}}$ and a base of $\lambda/2$. For such a wave the form factor $k_{\text{В}}$ is equal to the quadruplicated cosine of angle of triangle side inclination (dashed line), i.e. describes the "steepness" of wave edge. Because of $\nu = v_{\text{В}}/\lambda$, the wave energy $E_{\text{В}}$ can be expressed as

$$E_v = 8\rho \, v_{\text{В}}^2 \, k_{\text{В}}^2, \tag{15.1.5}$$

i.e. as the function of wave form and phase velocity.

Thus the steeper the wave edge, the greater the wave influence on matter. This is not the least of the factors to explain the specific character of waves forming in spark dischargers.

It is significant that all the consequences from the energodynamic consideration of the field energy forms are not based on whatever model representations of ether and physical vacuum, structure and properties of "field-forming" material objects, as well as origin of "particles" carring energy in space. This imparts the required generality to the conclusion about unity for the field forms of energy and their transfer processes. The appropriateness of considering the wave form of energy in the same rank with the force fields is confirmed by experimental data evidencing the existence of "solitary" waves (solitons) having the properties of particles. This provides a natural explanation for the wave-particle dualism and removes a major part of difficulties stated here for theoretical physics. The heuristic value of studying the field forms of energy will also be confirmed hereafter by multiple example of "over-unity" devices which operaion can be easily explained by disturbed equilibrium between field and matter and by energy exchange arising between them.

15.2. Energy Transfer at Force Field Deformation. Potential Retardation

Comprehending that fields are generated by not the charges, masses or currents, but by their heterogeneous distribution in space enables a new view for the long-history problem of the “retarded potential”. It is quite evident that as any of the “field-forming” bodies or charges are moving the fields “deform”, i.e. not only the field strength in the same points of space varies, but also the field configuration as defined by field heterogeneity. Since the propagation velocity for such field disturbances is finite, the field influence on test bodies or charges occurs with some retardation.

C. F. Gauss was the first who contemplated the consequences of that phenomenon later called the “potential lag”. In 1835 he discovered the law of magnetic interaction dynamics, which considered the relative velocity **v** of the interacting charges. He reckoned that if the rate of propagation of the interaction potential was finite, then it reached the moving body with some lag. This lag increases with increasing the velocity $v_r \equiv dr/dt$ of the bodies moving away from each other along the line connecting them. When the velocity v_r reaches the interaction propagation rate c for a particular medium, the force $\mathbf{F}_e$ one charge Θ_e' acts on the other Θ_e, becomes equal to zero, which is the fact that must be considered in the law of the charge interaction:

$$\mathbf{F}_e = \frac{\Theta_e \Theta_e'}{4\pi\varepsilon_o r^2}\left(1 - \frac{3v_r^2}{2c^2} + \frac{v^2}{c^2}\right), \qquad (15.2.1)$$

According to this equation the potential lag coefficient with bodies uniformly moving away is equal to $3v_r^2/2c^2$, where c – interaction propagation rate for a particular medium, which depends on the interaction mechanism. Since this mechanism is unknown, empirical laws are needed, which would enable checking the regularities found heuristically. E.g., Ampere’s law for interaction of two current-carrying conductors could become such empirical law. So the first step was essentially made from electrostatics to electrodynamics.

However, Gauss died and failed to publish his discovery. He could but send a letter to Weber, where he described his consideration on that point. Weber, who obviously did not approve the Gauss’s reasoning, published in 1846 instead of the Gauss’s formula his own law of electrodynamics in the form:

$$\mathbf{F}_e = \frac{\Theta_e \Theta_e'}{4\pi\varepsilon_o r^2}\left(1 - \frac{v_r^2}{2c^2} + \frac{ar}{c^2}\right), \qquad (15.2.2)$$

where Θ_e, Θ_e' – interacting point charges, C; r – distance in-between them; $v_r^2/2c^2$ – lag coefficient; ar/c^2 – coefficient of the radiation caused by the charge acceleration $a = |\boldsymbol{a}| = d^2r/dt^2$.

Weber represented this relationship as some formalism without revealing the cause-effect chains it contains. In particular, he interpreted the value “c” as a coefficient of conversion from the electrostatic to electrodynamic system of units. The true sense of expression (15.2.2) as an action lag law remained not quite clear even after Weber together with Kohlrausch had experimentally shown the equality of the coefficient “c” to the velocity of light for electromagnetic phenomena. Therefore, Helmholtz and Maxwell, two outstanding physicists of that time, interpreted the Weber’s formalism as a reflection of the long-range action law incriminating it as a violation of the energy conservation law and harshly criticized it. However, after Weber had published the Gauss’s letter in his collection of scientific papers in 1867, Maxwell having acquainted with Weber’s reasoning changed his opinion and dedicated the whole chapter to the lag phenomenon in his “Treatise on Electricity”. He showed there that both laws – Gauss’s and Weber’s – were derived from Ampere’s law and within the short-range action concept did not contradict the energy conservation law. Maxwell, the first who perceived that light was electromagnetic oscillations, correctly interpreted Weber’s law having indicated its connection with the “potential lag” phenomenon.

In 1898 P. Gerber as a result of the similar reasoning regarding the gravitational potential lag obtained a new law similar to the law of Weber’s electrodynamics:

$$\mathbf{F}_m = \frac{M \cdot M'}{r^2}\left(1 - 3\frac{v_r^2}{c^2} + 6\frac{ar}{c^2}\right) \qquad (15.2.3)$$

where M, M' – masses of the interacting bodies. This expression corresponds to the gravitational potential in the form:

$$\varphi_g = \frac{M'}{r(1 - v_r / c)^2} \qquad (15.2.4)$$

According to Gerber the potential lag per unit time is proportional to the multiplier rv_r/c. A somewhat different result will be obtained if proceeding from the Lorenz-invariance of Maxwell’s laws (R. Feynman, 1977):

$$\varphi_e = \frac{\Theta_e{}'}{4\pi\varepsilon_o(r - \mathbf{v}\cdot\mathbf{r}/c)_{\text{lag}}} \quad . \qquad (15.2.5)$$

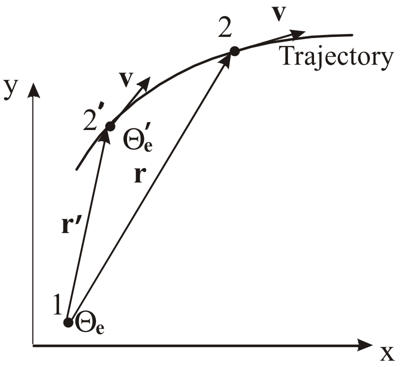

Fig. 15.2. Potential Lag Occurring

Here all the values in brackets (distance r to test charge, velocity **v** of field-forming charge, vector direction **r**) are calculated at the “lagging” instant of time *t*'. This potential is named the Lienar-Vihert potential. This, as well as (15.2.4), assumes the vector **r** direction toward the test charge to be the positive direction. According to (15.2.5) the field potential increases when two point charges are moving toward each other ($\mathbf{v}\cdot\mathbf{r} > 0$) and decreases when those are moving away from each other ($\mathbf{v}\cdot\mathbf{r} < 0$). However, this decrease does not lead to the potential becoming zero at v/c = 1, which contradicts the Gauss’s standpoint. Furthermore, when the charges are moving toward each other with a velocity of c, this potential becomes equal to infinity.

Due to the unacceptability of both results it is reasonable to clarify the notion of potential retardation. Like the relief, the field and its potential themselves move to nowhere and can only change with time. Therefore the stationary fields never and to nowhere “retard”. Only the *variations* of potential caused by the relative movement of any of the field-forming bodies, charges and currents or by their variation with time, i.e. the field *deformations*, can “retard”. Strictly speaking, this refers to the test charges, too, since the ratio of the force $\mathbf{F}_e$ to their value Θ_e is defined for them by the same field potential[1].

Because both of the results are unacceptable, it is advisable to clarify what the potential lag means. Like a relief, the potential as itself moves nowhere and, therefore, never lags. Only the potential *variations* caused by the relative displacement of each of the field-forming bodies or charges may “lag”, i.e. the field *disturbances*.

Let a field-forming body with a charge of Θ_e' move along an arbitrary path 2'–2 (Fig. 15.2). Let us assume that at some instant *t'* when the

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[1] Here the conditionality of the notion of “test” charge or body as values not causing field deformation shows up.

distance in-between the body and the test charge Θ_e' is equal to r' these start moving away from each other along the line connecting them with a velocity of $v_r = \mathbf{v}\cdot\mathbf{r}/r$. In this case the true value of the lag Δt can be calculated as the sum of the elementary lag times $dt = dr/(c_i - v_r)$ found by the absolute velocity $(c_i - v_r)$ of spreading the front of this disturbance out in space:

$$\Delta t = \int \frac{dr}{c_i - v_r} = \frac{r}{\bar{c}_i - \bar{v}_r}, \qquad (15.2.6)$$

where $\bar{c}_i, \bar{v}_r$ – mean velocities of spreading the interaction in a particular medium and moving the charges or bodies away from each other, respectively.

According to this expression the potential lag is absent, if the bodies are mutually immobile ($r = r'$) or there is no field variations (disturbance and its displacement are absent and $dr = 0$). Furthermore, Furthermore, it becomes infinity when $\bar{v}_r = \bar{c}_i$, which meets the Gauss's ideas as well. This principally distinguishes expression (15.2.5) from the preceding ones, where the lag was taken equal to $\Delta t = t - t' = r'/c$, i.e. was always different from zero, did not depend on the relative velocities of the bodies or charges and, against Gauss, did not become infinite when the velocity v_r of the bodies moving away became equal to the velocity c_i of spreading the interaction of a particular kind.

Let us assume that at some instant t' when the distance in-between the body and the test charge Θ_e' is equal to r' these start moving away from each other along the line connecting them with a velocity of $v_r = \mathbf{v}\cdot\mathbf{r}/r$. In this case the true value of the lag Δt can be calculated as the sum of the elementary lag times $dt = dr/(c_i - v_r)$ found by the absolute velocity $(c_i - v_r)$ of spreading the front of this disturbance out in space:

$$r' - r = \bar{v}_r \Delta t. \qquad (15.2.7)$$

It is the interval Δt that will become the lag time of *variations* of the potential $\varphi(\mathbf{r},t)$ considered as a function of current state, i.e. the field coordinate $\mathbf{r}$ and the current instant t. The value of this "lagging" potential, as can be easily seen, is defined by its magnitude $\varphi(\mathbf{r}',t')$ at some preceding instance t' when the distance in-between the bodies was r'. Considering (15.2.5) and (15.2.6) jointly gives:

$$r' = \frac{r}{1 - \bar{v}_r / \bar{c}_i} \qquad (15.2.8)$$

Due to this connection between the current and "lagging" positions of the interacting bodies or charges the value of the "lagging" potential $\varphi(\mathbf{r},t)_{\text{lag}}$ at the instant t is defined by its "preceding" magnitude $\varphi(\mathbf{r}',t')$ multiplied by the fudge factor $(1-\overline{\mathrm{v}}_{\mathrm{r}}/\overline{\mathrm{c}}_{\mathrm{i}})$:

$$\varphi(\mathbf{r},t)_{\text{зап}} = \varphi(\mathbf{r}',t')(1-\overline{\mathrm{v}}_{\mathrm{r}}/\overline{\mathrm{c}}_{\mathrm{i}}). \qquad (15.2.9)$$

This potential differs from the Lienard-Wiechert potential because at $\mathrm{v}_{\mathrm{r}} = \mathrm{c}_i$ it becomes zero, but not infinite. In this case the force $\mathbf{F} = -(\partial\varphi/\partial\mathbf{r})$ acting on the test charge from the field will become zero in both cases – with the field-forming body moving away from the charge and with the test charge moving while the field-forming charge varies only with time. This completely conforms with Gauss. It is natural that with the field reduction the field-caused acceleration of the test charge will be also reducing. In the special relativity theory (SRT) this phenomenon is interpreted as the growth of test body mass M relative to the rest mass M_{o}. However, in view of the ideas expounded such a growth of mass up to infinity is only apparent, while the point of the phenomenon lies in the reduction of the force and acceleration of the charge this force causes.

Another difference from the Lienard-Wiechert potential is that the expression (15.2.9) operates the mean velocities of the body–wave front relative motion, whereas in (15.2.2) and (15.2.3) for definition of the force **F** as a derivative of the potential φ the acceleration of charges or bodies is considered. It is quite evident that when the resultant motive force **F** becomes zero an acceleration of charges or bodies is impossible so that in expressions (15.2.2) and (15.2.3) at $\mathbf{F} = 0$ the acceleration-containing term should have disappeared regardless the values of other terms. In other words, the possible non-uniformity of the relative motion of charges or bodies, as well as of the velocity of interaction spreading in a heterogeneous medium should not tell on the value of the lagging term which according to (15.2.6) depends on only their mean values.

Not less important should be the fact that expression (15.2.8) contains not the velocity of light c in vacuum, which is constant, but the velocity c_{i} of interaction spreading in a particular medium. This depends on the properties of the material medium where the i^{th} kind interaction is spreading, on the relaxation process "mechanism", on the field nature, etc. This is especially evident from the positions of energodynamics, according to which the force fields are generated by not bodies, charges or currents as themselves, but their non-uniform distribution in space. In such a case any variation of the field results from the redistribution of the bodies, charges and currents in the space filled with a field-forming substance. The rate of this process generally differs from the rate of electromagnetic interaction spreading in the void. E.g. for the magnetic field formed by two mutually moving permanent magnets it may be limited to the rate of reorientation of magnetic domains in them and be many orders lower than the velocity of light in vacuum. In this case the potential lag effect will show at not only the so-called “relativistic” velocities comparable with the velocity of light in vacuum, but even at moderate velocities of the magnets moving relative to each other.

This fact casts a new light on the “self-sustained rotation” effect, which defies a theoretical explanation and was first discovered by J. Serl (Switzerland) in the fifties of the last century. This effect consists in perpetual rolling of magnetic rolls on the cylindrical surface of a multilayer or segmented permanent magnet after imposing a minor momentum on one of these rolls. That effect was later observed in the experiments of V. Roshchin and S. Godin, who constructed in 1992 a generator they called the “magnetodynamic converter” – similar to the Serl’s one, with a 350 kg self-rotating rotor, and also in the experiments with the self-rotating Hamster wheel. It is important that the “self-sustained rotation” phenomenon stably shows in also the electrostatic current generators “Testatica” which are a modernized electroforous Wimshurst generator. This phenomenon appears at certain conditions in also the magnetic motors, which rotor and stator are a set of permanent magnets similar to the magnetic track of the Minato wheel (see Chapter 22). In the last case the torque appeared is especially evident and explained by the change of the velocity sign in (21.2.8) with the permanent magnets moving toward and subsequently away from each other, which causes inequality of the attractive and repulsive forces. A new understanding of this phenomenon and the justified possibility of its appearance at yet moderate rates of the relative motion may contribute to its even wider practical application.

15.3. Maxwell’s Equations Generalization Allowing for Displacement Fluxes of Bound Charges

The displacement currents are generally assumed to enter in the right-hand side of Maxwell’s equations (8.2.18) and (8.2.19) on absolutely equal terms with the transfer current. However, “no one has been solving these equations in terms of displacement currents up to date because these solutions have appeared to be just impossible” (R. Feynman and others, 1977). In our opinion, the reason is that the consideration of the displacement currents in the Maxwell’s equations is just apparent. In fact, the concept of flow having come from mechanics is closely connected with the idea of liquid streaming and its momentum available. In particular, in the TIP the electric current density is defined by the product of the electric charge density ρ_e and the charge transfer velocity $\mathbf{v}_e$. However, in the theory of electromagnetism the displacement currents are expressed in terms of the partial derivative ($\partial\mathbf{E}/\partial t$) of the field intensity vector **E**, which "can not be construed as the rate of something" (R. Feynman and others, 1977). This shows especially evident in the thermodynamic derivation of the Maxwell's equations in the previous paragraph.

Let us expand the derivative $d\mathbf{D}/dt$ in (8.2.4) considering all the charges available in the system (both the free ρ_e and the polarization $\rho_e' + \rho_e''$ ones). Taking into account the identity of the induction vector **D** to the distribution moment $\mathbf{Z}_{ev}$ and comparing the expression $\nabla\cdot\mathbf{Z}_{ev} = \rho_e + \rho_e' + \rho_e''$ with the expression $\mathbf{D} \equiv \varepsilon_o\varepsilon_r\mathbf{E} + \mathbf{P}$ gives that $\rho_e = \varepsilon_o\varepsilon_r \nabla\cdot\mathbf{E}$. Thus the Gauss's law

$$\nabla\cdot\mathbf{E} = \rho_e/\varepsilon_o\varepsilon_r \qquad (15.3.1)$$

may be derived without applying to the extremely abstract idea of the "field flow".

Let us further take into account that according to (8.2.4) the total time derivative of the electric induction **D** vector in dielectrics includes, besides the local component ($\partial\mathbf{D}/\partial t$) and the component $\varepsilon_o\varepsilon_r(\mathbf{v}_e\cdot\nabla)\mathbf{E} = \mathbf{j}_e$, caused by the conduction current $\mathbf{j}_e$, one more component $\nabla\cdot\mathbf{P} = (\mathbf{v}_e'\cdot\nabla)\mathbf{P} + (\mathbf{v}_e''\cdot\nabla)\mathbf{P} = \mathbf{j}_e' + \mathbf{j}_e''$, caused by the transfer of dipole charges in accordance with (8.4.4). Considering this component called for short the polarization one gives:

$$d\mathbf{D}/dt = (\partial\mathbf{D}/\partial t) + \mathbf{j}_e + \mathbf{j}_e' + \mathbf{j}_e'', \qquad (15.3.2)$$

Likewise, according to (8.2.4) let us expand the derivative $d\mathbf{B}/dt$ taking into account that $\nabla\cdot\mathbf{H} = 0$ and that according to (8.4.3) and (8.4.5) $\nabla\cdot\mathbf{B} = (\mathbf{v}_M'\cdot\nabla)\mathbf{M} + (\mathbf{v}_M''\cdot\nabla)\mathbf{M} = \mathbf{j}_M' + \mathbf{j}_M''$. Due to the existing polarization component of the magnetic displacement flux $\mathbf{j}_M' + \mathbf{j}_M''$ along with $\nabla\cdot\mathbf{B} = 0$ it follows that

$$d\mathbf{B}/dt = (\partial\mathbf{B}/\partial t) + \mathbf{j}_M' + \mathbf{j}_M'' \qquad (15.3.3)$$

In essence, the right-hand side of (15.3.3) considering the polarization component of displacement flux is also the total "magnetic flux" $\mathbf{j}_M^t$ that differs from $\mathbf{j}_e^t$ by only the absence of the conduction current analog. In the general case, when a non-uniformly polarized dielectric is moving in space with a velocity of **v**, the magnetic displacement flux $\mathbf{j}_M'$ and $\mathbf{j}_M''$ may also be represented as the sum $\mathbf{j}_{\text{M}}' = \rho_{\text{M}}'(\mathbf{v}_{\text{M}}' - \mathbf{v}) + \rho_{\text{M}}'\mathbf{v}$ and $\mathbf{j}_{\text{M}}'' = \rho_{\text{M}}''(\mathbf{v}_{\text{M}}' - \mathbf{v}) + \rho_{\text{M}}''\mathbf{v}$ thus highlighting there the "convective" component $\mathbf{j}_{\text{M}}^{\text{c}} = (\rho_{\text{M}}' + \rho_{\text{M}}'')\mathbf{v}$ caused by the movement of the magnetic as a whole. In this case the components $\rho_{\text{M}}'(\mathbf{v}_{\text{M}}' - \mathbf{v})$ and $\rho_{\text{M}}''(\mathbf{v}_{\text{M}}' - \mathbf{v})$ will appear as the displacement fluxes of the poles relative to their common center, while the values $\mathbf{j}_{\text{M}}'$ and $\mathbf{j}_{\text{M}}''$ will take the meaning of the sum of the convective flux and the displacement one, which may be called by analogy the total magnetic displacement flux $\mathbf{j}_{\text{M}}^{\text{t}}$.

Given (15.3.2) and (15.3.3), Maxwell's equations (8.5.18) and (8.5.19) for moving bodies may be rewritten as:

$$\text{rot}\,\mathbf{E} = \mathbf{j}_{\text{M}}^{\text{п}} - (\partial\mathbf{B}/\partial t), \qquad (15.3.4)$$

$$\text{rot}\,\mathbf{H} = \mathbf{j}_{\text{e}}^{\text{п}} + (\partial\mathbf{D}/\partial t), \qquad (15.3.5)$$

These expressions differ from the corresponding Maxwell's equations by taking into account the polarization component of the electric and magnetic displacement fluxes. This further contribute to the similarity of electric and magnetic phenomena, especially with Maxwell's equations written as (8.5.15) and (8.5.16), and makes this "duality" even more complete.

Explicit consideration of the polarization displacement fluxes in the equations of electromagnetic field eliminates a number of difficulties electrodynamics suffers, in particular, those of them which are attributed to known exceptions from the flux regulations (R. Feynman and others, 1977). According to (8.5.11) and (8.5.12) the electromotive and magnetomotive forces appear not only due to variations of the electric **D** and magnetic **B** induction vectors, but also due to the energy carrier flows (electric and magnetic charges) irrespective of what causes these flows – either the redistribution of the charges in the system or the motion of the system itself. This explains why EMF appears where the "flux" $\partial\mathbf{B}/\partial\text{t}$ does not vary and never appears where this flux varies (see the examples with the flux through the rotating disc and with the tilting plates as given by R. Feynman, 1977). This excludes the necessity he noted in using the various laws of force for the case of the closed circuit moving and the field varying.

The fact that the displacement fluxes in their physical meaning are taken into account in the field equations easily explains why the electric polarization appears in moving magnetic in the absence of the external field **H**. The derivative $(\partial\mathbf{D}/\partial t)$ being different from zero is caused in this case by the available convective component $\mathbf{j}_{\text{e}}^{\text{c}}$ of displacement current, which is connected with the movement of the electrified body. From these positions the magnetic field generation with a polarized dielectric moving

(Rowland–Eichenwald and Röntgen–Eichenwald effects), as well as the polarization of a dielectric plate when moving in the magnetic field (Wilson–Barnet effect) are also explained as the consequence of $\mathbf{j}_e^c$ without appeal to the relativistic transformations. In particular, it becomes clear that even in uniformly polarized bodies in the presence of the "convective" component $\mathbf{j}_i^c = (\rho_i' + \rho_i'')\mathbf{v}$ the different-directed displacement fluxes $\mathbf{j}_e'$, $\mathbf{j}_e''$ and $\mathbf{j}_M'$, $\mathbf{j}_M''$ become different in their values. This fact may directly pertain to the "self-movement" of ferromagnetics after a starting impact (Serl effect) observed by many investigators.

Let us make sure now that the equations obtained are internally consistent. Taking the divergence of both sides of (15.3.5) and considering that the rotor divergence is equal to zero gives:

$$\nabla\cdot\mathbf{j}_e + \nabla\cdot(\mathbf{j}_e'+\mathbf{j}_e'') + (\partial^2\mathbf{D}/\partial\mathbf{r}\partial t) = 0. \tag{15.3.6}$$

The derivation sequence for coordinates and time may be swapped in the last summand:

$$\nabla\cdot\mathbf{j}_e + \mathrm{div}\,(\mathbf{j}_e'+\mathbf{j}_e'') + (\partial^2\mathbf{D}/\partial t\partial\mathbf{r}) = 0. \tag{15.3.7}$$

Since $\nabla\cdot\mathbf{D} = \rho_e + \rho_e^{п}$, the last term in (15.3.7) is the sum of the derivatives $(\partial\rho_e/\partial t)$ and $(\partial\rho_e^t/\partial t)$, so that this relationship becomes:

$$[(\partial\rho_e/\partial t) + \mathrm{div}\,\mathbf{j}_e] + [(\partial\rho_e^{п}/\partial t) + \mathrm{div}\,\mathbf{j}_e^c] = 0, \tag{15.3.8}$$

Both sums in square brackets are the balance equation in the general form $(\partial\rho_i/\partial t) + \mathrm{div}\,\mathbf{j}_i = 0$ and become zero (the first sum – according to the charge conservation law, while the second one – owing to the fact that the appearance of the dipole charge is caused by exclusively the spatial separation of the dipole poles and, therefore, by the fluxes of their displacement appearing). Thus equation (21.3.5) is satisfied.

To make sure that equation (15.3.4) is internally consistent, let us take the divergence of its both sides and repeat the operations of (15.3.6)–(15.3.8):

$$\nabla\cdot(\mathbf{j}_M'+\mathbf{j}_M'') + (\partial^2\mathbf{B}/\partial\mathbf{r}\partial t) = \nabla\cdot(\mathbf{j}_M'+\mathbf{j}_M'') + \partial\rho_e^{п}/\partial t = 0. \tag{15.3.9}$$

As can be seen, this expression as well corresponds to the balance equation without sources. However, now it is caused by not the "magnetic" charge conservation, but by the fact that the appearance of the magnetic dipoles is also inseparably linked with the spatial separation of the unlike poles, i.e. with the divergence of fluxes of their displacement. Thus the total derivatives of electric **D** and magnetic **H** induction vectors being available in the electromagnetic field equations as imposed by the thermodynamic relations for dielectrics and magnetics are internally consistent. This makes us be more respectful to the experiments on creating energy converters of the electromagnetic fields surrounding us, which results do not keep within present electrodynamics.

15.4. Possibility of Single-Wire Energy Transmission

The Maxwell's equations describe the energy conversion processes in closed electric and magnetic circuits. Therefore only closed two-wire circuits are considered for the energy transmission in electrical engineering, whereas the single-wire energy transmission is deemed impossible. Meantime, yet in 1892-93 N. Tesla demonstrated a single-wire energy transmission in London and Philadelphia. In that case the Earth itself was the conductor. No information remained on the technical part of that experiment. However, in 1978 S.V. Avramenko, a researcher of one of the research institutes in Moscow, demonstrated the possibility to transmit alternating current via a single wire without earthing (1991).

His device is based on the "Avramenko's plug" (GB Patent PCT/GB93/00960, 1993), which is two in-series semiconductor diodes (Fig.15.3).

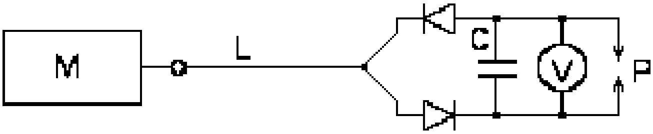

Fig.15.3. Single-Wire Energy Transmission Schematic by Avramenko S.V.

If the plug is connected to a lead under practically any alternating voltage (10 V thru 10.000 V), then after a while there will be serial sparks observed in the discharger P. By this way an active power of 1.3 kW can be successfully transmitted via a single tungsten wire with a diameter of 20 μm. Even a resistor rated 2-5 MΩ included in the transmission line does not substantially changes the circuit operation. The transmission efficiency measured in one of the tests by wattmeters on a generator frequency of 8 kHz and confirmed with calculations by the formulas I_2U_2 or I_22R_2 was 0.72. Now the author transmits the energy within a distance of 160 m (N. Zaev, 1994).

The possibility of the single-wire energy transmission as based on the Avramenko's invention has been confirmed by the experiments of S. Hartmann and N. Kosinov. In the Hartmann's generator a car ignition coil is used, while the electronic generator itself operates on a frequency of 10 kHz. A xenon flash lamp is used as load, while a copper wire – as antenna (N. Zaev and others, 1991).

In the N. Kosinov's arrangement the traditional bridge circuit is used (Fig.15.4) instead of the "Avramenko's plug". The power supply Б5-47 serves as energy source, while the incandescent lamp with a power of 25 W – as load.

Some investigators of this phenomenon deduce it from the "physical vacuum energy recovery", "line superconductivity" and even "generation of *information* by power supply". Not more successfully it can be explained by the polarization current existing since these currents are local and absent in metals. Quite other prospect opens from the positions of energodynamics having proved the existence of the displacement current convective component with a density of $\mathbf{j}_e = \rho_e \mathbf{v}_e$ (21.3.3). As shown above, this current exists together with the one caused by the polarization charges moving and is conditioned by redistribution of the free electric charge over the system volume (in this case – the single-wire line). For metals $\mathbf{P} = 0$ and according to (15.3.3)

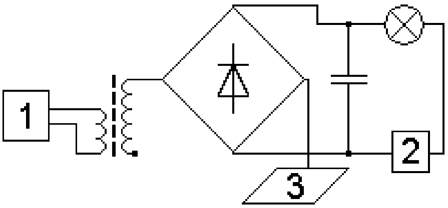

Fig.15.4. Circuit Schematic by N. Kosinov.
1 – Generator, 3 – "Antenna"

$$d\mathbf{D}/\mathrm{d}t = (\partial \mathbf{D}/\partial t) + \mathbf{j}_e^c. \qquad (15.4.1)$$

In addition to the displacement current in its traditional interpretation ($\partial \mathbf{D}/\partial t$), this expression includes the displacement current "convective" component $\mathbf{j}_e^c$. The only difference of this current from the usual conduction current is that it does not cross the system boundaries, i.e. is "internal". The energy transfer via the single-wire line looks like the following: during that half-period of voltage oscillation at the power supply (generator) output when the input potential to the single-wire line decreases, the free charge local density ρ_e in this line decreases correspondingly. This means there is a redistribution of the charge occurring in the line with its displacement toward the end of the line shown on Fig.15.4. The gate opened in this direction lets this displacement current through, which leads to increasing the potential on the end of the line. In the returning pulse, on the contrary, the charge outflows and the potential decreases on the end of the line. Being gradually accumulated, this charge and its potential cause spark gap breakdown, incandescent lamp glow, power release in the load, etc, quite in the same way as in the two-wire line operation. However, the current in the single-wire line is in this case several orders lower, which can be illustrated by the following example. Let us assume that in a usual two-wire line the resistive load receives the power $N = 1$ kW with a current in the line and the load of 1 A. For this it is necessary to create in the load and the line a voltage of 1,000 V. To build up the potential on the output end of the single-wire line by the same value 1,000 V due to displacement currents, it is enough to create in it an excess charge of 10^{-6} C (as compared with the opposite end of the line). This is what explains the results of the experiments, according to which, to transmit a power in excess of 1 kW, a lead with a diameter of 20 μm appears to be enough, whereas an additional resistance of 2 MΩ included in the line does not noticeably influence. Thus energodynamics lifts a ban for the single-wire energy transmission.

15.5. Longitudinal Electromagnetic Waves Existing

The existence of waves called by different authors the electromagnetic waves in conducting media, multipolarized electromagnetic waves, longitudinal electric waves, longitudinal magnetic waves, etc, have been lately arousing ever growing interest, winning the recognition and experimental validation. These are waves, where the medium oscillates in the direction of their propagation. Ampere was the first suggested the existence of such waves based on his in-depth analysis of one of the paradoxes in electrodynamics associated with the violation of the third law of mechanics. However, against the common recognition and triumph of the Maxwell’s equations, such paradoxes were not subjected to a theoretical analysis detailed enough. Maxwell himself, who predicted the existence of electromagnetic waves, is known to have denied in theoretical discussion the existence of a unidirectional vector field induced by the “density” pulsation of the electrostatic fields similar to the pressure pulsations in the acoustic waves. Such pulsations would mean there is a variable concentration of the electrostatic field force lines spreading along the electrostatic field lines. Therefore the Maxwell’s equations did not contain solutions corresponding to those waves and all subsequent efforts of experimenters were mostly directed to reveal the transverse waves, i.e. the waves where the electric and magnetic fields are directed perpendicular to the direction of their propagation. H. Herzt was the first who reported in 1887 such waves had been experimentally discovered. However, as N. Tesla demonstrated two years later, the effects Hertz had observed might be caused by the longitudinal waves as well which consisted of a sequence of the unidirectional shock waves caused by the interruption of the electrostatic field and capable to act on the charges in the direction of their propagation. One way or another, some types of the longitudinal waves have been known long enough. Such are, e.g. the Langmuir waves induced by the collective oscillations of bulk charge in the plasma. The longitudinal electromagnetic waves investigators have been discovered in wave conductors, resonators, piezoelectrics, semiconductors, liquid crystals, single-wire energy transmission lines, etc, are another type. There is also a special class of transmitting-receiving antennas (the so-called EH-antennas that emit evidently the longitudinal waves and provide communication through water and rock masses (L. Strebkov, S. Avramenko and others, 2004).

Voluminous literature is presently dedicated to investigation of the longitudinal electromagnetic waves (LEMW). LEMW generators, transversal-into-longitudinal wave converters, detectors, mixers and power meters have been created (S. Abdulkerimov, Y. Ermolaev, B. Rodionov, 2003). As the generators in various devices are the radial-flux plasma, gas discharge tube, quarter-wave resonator, etc. Such waves are registered by the Schottky-barrier diode, photomaterials protected with foil-covered light-tight screen, liquid-crystal indicators, phase-contrast microscopy of high-clean water, etc. Four types of electric and magnetic longitudinal waves have been lately studied with a special ardor, viz. a) longitudinal electric wave (in the **E** direction); b) longitudinal magnetic wave (in the **H** direction); c) torsion wave (along **H** with the vortex component **E**); d) Tesla wave (along **E** with the vortex component **H**).

The experiments have revealed a number of unusual properties of the longitudinal electromagnetic waves (LEMW). They demonstrate high penetrability and are detected through water and rock masses, metal and reinforced concrete (D. Strebkov, S. Avramenko and others, 2004). LEMW propagate in small-diameter tubes bent at any angle or twisted in spirals, slits and thin water layers, along the boundaries of free charges-containing media, etc. LEMW flows may be split in parts and collected in corresponding devices. In this case the losses on resonance frequencies are orders lower in LEMW than in usual electromagnetic waves (S. Abdulkerimov, Y. Ermolaev, B. Rodionov, 2003).

According to the available theoretical speculations the LEMW propagate in dielectrics with a velocity of v_h considerably exceeding the velocity of light ($v_h / c = 1.87 \cdot 10^4$), high wave resistance (2.2 MΩ) and are directly related to the informational transfer to a particular point long before the transverse electromagnetic wave comes. This is the fourth kind of these waves N. Tesla is also assumed to have used in his experiments on the energy transfer through the ground. The Tesla's longitudinal wave is an analog of the longitudinal acoustic wave and propagates with minor losses in solid, liquid and gaseous conducting media. The heat losses are practically absent in this case. It is this kind of the longitudinal wave that evidently appears in the Avramenko's circuit causing the energy transfer via the single-wire line (see the previous paragraph).

At these conditions to reconcile the fact of existing longitudinal electromagnetic waves with the Maxwell's equations becomes of special importance. As mentioned above (Chapter 8), if two sets of unlike bulk charges can penetrate into each other, then with their centers registered the potential of the system becomes equal to zero. When a dielectric or magnetic appears to be in the external electric **E** or magnetic **H** field, the redistribution of bulk charges occurs resulting in the formation of two subsystems, each having its own "dipole" (electric ψ_e', ψ_e'' or magnetic ψ_M', ψ_M'') potential [1]. As a result, the internal electric **E**' or magnetic **H**' field appears, which being added to the external field gives a resultant "induced" field defying the stressed state of the dielectric or magnetic. From the positions of energodynamics this state is characterized by the extensive parameters $\mathbf{Z}_e$ and $\mathbf{Z}_M$ related with the intensive variables **E**' and **H**' by the equations of state and defying the polarization or magnetization of the system as a whole (V.V. Sychev, 1977). In electrodynamics using traditionally only the intensive variables, instead of $\mathbf{Z}_e$ and $\mathbf{Z}_M$ their values in dielectric or magnetic unit volume are applied called the vectors of electric **D** and magnetic **B** induction, respectively. These are connected with the intensities of external field **E** or **H** and the vectors of polarization **P** and magnetization **M** corresponding to the fields **E**' and **H**' by the equations of state (8.2.4).

As follows from the above, the specificity of polarized media is that they have two subsystems with opposite properties (in our case – with the unlike charges or poles ρ_e', ρ_e'' and ρ_M', ρ_M''). It is important that these charges appear as not a result of the heterogeneous polarization, but insofar as the polarization itself exists, i.e. when the arms of electric or magnetic dipoles are different from zero. In the general case of moving dielectrics or magnetics these two subsystems behave independently and move in space with the different velocities $\mathbf{v}_e'$, $\mathbf{v}_e''$ and $\mathbf{v}_M'$, $\mathbf{v}_M''$. The associated processes of redistribution of the polarization charges have their own coordinates, viz. the displacement vectors $\Delta\mathbf{R}_i'$, $\Delta\mathbf{R}_i''$ (or their local analogs $\Delta\mathbf{r}_i'$, $\Delta\mathbf{r}_i''$).

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[1] The notion of magnetic potential reflecting the similarity (duality) of electric and magnetic fields and their equations has presently become quite widespread (L. Landau, E. Livshitz, 2004; K. Polivanov, 1982).

According to the theorem of degrees of freedom this means that the vectors of polarization **P** and magnetization **M** of the polarized media as a whole are functions of both $\Delta\mathbf{r}_i'$, and $\Delta\mathbf{r}_i''$, i.e. $\mathbf{P} = \mathbf{P}(\mathbf{r}_e', \mathbf{r}_e'', t)$ and $\mathbf{M} = \mathbf{M}(\mathbf{r}_M', \mathbf{r}_M'', t)$. In such a case, as shown in Chapter 8, the derivatives $\partial\mathbf{P}/\partial\mathbf{r}_e'$ and $\partial\mathbf{P}/\partial\mathbf{r}_e''$, as well as $\partial\mathbf{M}/\partial\mathbf{r}_M'$ and $\partial\mathbf{M}/\partial\mathbf{r}_M''$ in (8.4.2) and (8.4.3) are different from zero, while the total time variation of these vectors includes the polarization displacement fluxes $\mathbf{j}_e'$, $\mathbf{j}_e''$ and $\mathbf{j}_M'$, $\mathbf{j}_M''$. These fluxes being considered in Maxwell's equations (21.3.4) and (21.3.5) provide easy explanation on their basis that the longitudinal waves appear because the dipole charges Θ_i' and Θ_i'' can oscillate along the line connecting them, which results in appearing longitudinal waves coinciding in direction with the corresponding field vectors (see Chapter 8). These waves may be electric or magnetic depending on the types of the dipoles. It is important that such waves are emitted in also the case when the sum of unlike dipole charges becomes zero, i.e. even in uniformly polarized media. Naturally, they appear in only restricted space, which is experimentally confirmed.

Note, this conclusion would be impossible if not to consider that dielectrics and magnetics have subsystems with unlike polarization charges. In fact, the electric and magnetic dipoles being deprived of their extent and the polarization or magnetization vectors being considered as functions of the field point radius-vector **r** and the time t, i.e. $\mathbf{P} = \mathbf{P}(\mathbf{r}, \mathrm{t})$ and $\mathbf{M} = \mathbf{M}(\mathbf{r}, \mathrm{t})$ gives

$$d\mathbf{P}/dt = (\partial\mathbf{P}/\partial t) + (\mathbf{v}_e\cdot\nabla)\mathbf{P} = (\partial\mathbf{P}/\partial \mathrm{t}), \qquad (15.5.1)$$

since $\partial\mathbf{P}/\partial\mathbf{r} = \rho_e^{t} = 0$ in the uniformly polarized media. In this case the displacement fluxes of the polarization charges in Maxwell's equations (15.3.5) disappear along with the possibility to explain on their basis all phenomena defying any theoretical explanation.

Thus the longitudinal electromagnetic waves existing in dielectrics follow from the Maxwell's equations (8.2.15), (8.2.16) providing the partial derivatives of electric and magnetic flux density vectors are replaced therein by their exact differentials. Then it is easy to show that

$$\nabla\cdot\mathbf{A} \neq 0 \qquad (15.5.2)$$

where **A** – vector potential connected with the magnetic flux density through the relation $\mathbf{A} = \mathrm{rot}\mathbf{B}$.

To make sure this relation is true, consider the sense of the vector potential $\mathbf{A} = (\mathbf{v}_e/\mathrm{c}^2)\varphi$ (Feynman, 1964). Then

$$\nabla\cdot\mathbf{A} = \mathrm{c}^{-2}\varphi\nabla\cdot\mathbf{v}_e + \mathrm{c}^{-2}\mathbf{v}_e\nabla\varphi, \qquad (15.5.3)$$

i.e. $\nabla\cdot\mathbf{A}$ in the homogeneous field of the electric potential $\nabla\varphi = 0$ is defined by the divergence of the bound charges velocity vector $\nabla\cdot\mathbf{v}_e$. Since the polarization process means exactly the displacement of the charges ρ_e' and ρ_e'' in the opposite directions with the velocity $\mathbf{v}_e' = -\mathbf{v}_e''$, the reason for the divergence $\nabla\cdot\mathbf{A}$ of the vector $\mathbf{A}$ is obvious.

Thus the electromagnetic oscillations in dielectrics generate longitudinal waves in the same natural way as transverse ones. The appearance of forces acting along a current-carrying conductor is connected with this phenomenon. This phenomenon was discovered obviously for the first time in the Aaronov-Bom’s experiment (1956). The experiments Japanese physicists conducted in 1982 confirmed that the field of the vector potential **A** was actually a single-valued physical parameter, i.e. defined by not only rot**A**, but div**A** as well. The presence of longitudinal forces acting on the electrons moving along the toroid axis and on a copper conductor was later discovered in the A. Solunin's experiments and confirmed in the S. Grano's experiments with a copper conductor that moved along the direction of the current in it (G. Nikolaev, 1997). The appearance of a longitudinal force was lately (2007) discovered also in A.K. Tomilin’s experiments.

It is worth noting that yet in 1974 the Austrian professor S. Marinov, to completely define magnetic field, suggested the scalar function $H = \mu_o^{-1}\,\nabla\cdot\mathbf{A}$ should be introduced. Later the same conclusion was made by a number of other investigators (H. Khvorostenko, 1992; Y. Kuznetsov, 1995; G. Nikolaev, 1997, E. Nefedov et al, 1998), who suggested the Maxwell’s electrodynamic equations should be supplemented by the gradients of the scalar electric and magnetic fields E_o and H_o:

$$\mathrm{rot}\,\mathbf{E} + \nabla E_o = -(\partial\mathbf{B}/\partial t), \qquad (15.5.4)$$

$$\mathrm{rot}\,\mathbf{H} - \nabla H_o = \mathbf{j}_e + (\partial\mathbf{D}/\partial t)\,. \qquad (15.5.5)$$

There are about a dozen of patents for “self-moving” devices operating supposedly on this principle. Thus energodynamics eliminates the contradiction between classic electrodynamics and a number of experimental results inexplicable from the Maxwell's equations.

Chapter 16

NEW METHOD OF SUPERPOSITION EFFECTS INVESTIGATION FOR IRREVERSIBLE PROCESSES

This chapter is dedicated to the development of a new method to investigate kinetics of transfer processes, which is based on the definition of an only (resultant) force for each independent process, which disappearance ceases the process. This method allows dramatically simplifying the thermodynamic description of irreversible processes and reducing the number of coefficients required for such a description. It casts new light on the origin of the so-called stationary superposition effects for dissimilar processes and allows finding them from the conditions of partial (incomplete) equilibrium as a result of mutual compensation of the components comprising this resultant force. Thereby a possibility opens to prognosticate the value of these effects from the known analytical expressions for these forces without applying to reciprocal relations and without phenomenological coefficients preliminarily defined.

The efficiency of the method proposed and the validity of the consequences obtained within energodynamics will be confirmed by a great number of experimental data.

16.1. Definition of Superposition Effects as Partial Equilibrium Conditions

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 J_i was linear with all the thermodynamic forces X_j acting in the system, i.e. they used the same Onsager's law (5.1.6) 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 (5.4.1) 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 $\mathbf{J}_{ij} = L_{ij}\mathbf{X}_j$:

$$\mathbf{J}_i = \Sigma_j \mathbf{J}_{ij} = \Sigma_j L_{ij}\mathbf{X}_j . \qquad (16.1.1)$$

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 J_i of any relaxation process in (5.1.3) have always the same sign. Therefore some of these flows 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 (16.1.1) 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 $J_{ii} = L_{ii} X_i$ and $J_{ji} = L_{ji} X_i$ of flows (16.1.1) are expressed in terms of the matching components J_{ii} and J_{ji} of the flow J_i:

$$L_{ii} = dJ_{ii}/dX_i\,;\; L_{ji} = dJ_{ji}/d\mathbf{X}_i\,. \tag{16.1.2}$$

According to (16.1.2) there is a simple relation between the diagonal L_{ii} and non-diagonal ("cross") coefficients L_{ij} of the transfer equations in matrix form:

$$L_{ji} = L_{ii}\,(dJ_{ji}/dJ_{ii})\,. \tag{16.1.3}$$

However, at X_j = const $dJ_{ji} = dJ_j$ and $dJ_{ii} = dJ_i$, therefore (16.1.3) may be changed to:

$$L_{ji} = L_{ii}\,(\partial J_j/\partial J_i)_{Xj}\,. \tag{16.1.4}$$

From this it follows that providing the flows J_i and J_j are not interconnected, the coefficients L_{ji}, at X_j = const, become zero along with the derivative $(\partial J_j/\partial J_i)_{Xj}$. This means that for the independent flows J_i and 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 X_i as matching the flow J_i no other force whatever can induce this flow providing it is truly independent. Since the independence of the flows J_i and 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:

$$\mathbf{J}_i = K_i(\mathbf{F}_i - \mathbf{F}_{io}) = L_i(\mathbf{X}_i - \mathbf{X}_{io}),\ (i = 1, 2, ..., n_i) \qquad (16.1.5)$$

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 $\mathbf{F}_i$. The principle difference of equations (14.1.5), besides their non-linearity and the "threshold" values of the forces $\mathbf{F}_{io}$ 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 $\mathbf{F}_{ij} = \Theta_j\mathbf{X}_{ij}$ as it takes place in the anisotropic heat conduction and electric conduction equations. Therefore laws (16.1.5) may be written in the form:

$$\mathbf{J}_i = K_i(\mathbf{F}_j)\, \Sigma_i\, \mathbf{F}_{ij},\ (i, j = 1, 2, ..., n). \qquad (16.1.6)$$

This form of transfer laws reflex the **force superposition principle**: *the rate of a process in the space of n variables is defined by the sum of projections of all forces acting in the system onto the direction of the process.* It is a matter of no small importance that the components $\mathbf{F}_{ij}$ of the resultant force $\mathbf{F}_j$ in equation (16.1.6) 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 (5.4.1) 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 (16.1.6) 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.

16.2. Theoretical Prognostication of Superposition Effects

The existing theory of irreversible processes (TIP) is known to find the superposition effects for dissipative processes by using the Onsager reciprocal relations and only for the so-called stationary states of various order. 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 (5.1.6). For the simplest case with two flows $\mathbf{J}_i$ and $\mathbf{J}_i$ these equations are:

$$\mathbf{J}_i = L_{ij}\,\mathbf{X}_i + L_{jj}\,\mathbf{X}_{j,} \tag{16.2.1}$$

$$\mathbf{J}_i = L_{ji}\,\mathbf{X}_i + L_{jj}\,\mathbf{X}_j\,. \tag{16.2.2}$$

From (16.2.2.) it follows, in particular, that for the state with $\mathbf{J}_i = 0$ the stationary effect is expressed by the relationship:

$$(\nabla\Psi_j/\nabla\Psi_i)_{\text{ст}} = -\,L_{ij}/L_{jj}\,. \tag{16.2.3}$$

As follows from (16.2.3), 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 (18.1.5). 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:

$$\mathbf{F}_i = \Sigma_j \mathbf{F}_{ij} = 0;\ \ \mathbf{X}_i = \Sigma_j\,\mathbf{X}_{ij} = 0. \tag{16.2.4}$$

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:

$$\mathbf{F}_i = \Theta_i\,\mathbf{X}_i + \Theta_j\mathbf{X}_j = 0, \tag{16.2.5}$$

which gives

$$(\nabla\Psi_j/\nabla\Psi_i)_{\text{ст}} = -\,\Theta_i/\Theta_j\,. \tag{15.2.6}$$

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.

16.3. Definition of Hard-to-Measure Thermodynamic Parameters Based on Superposition Effects

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:

$$\mathbf{J}_k = K_k \, \Sigma_i \, \mathbf{F}_{ki} = L_k \mathbf{X}_k. \tag{16.3.1}$$

In accordance with (5.5.6) 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:

$$d\zeta_k = d\mu_k + T ds_{ko}\,. \tag{16.3.2}$$

Considering (16.3.2) with the expression of exact differential of the chemical potential p,T,c_ℓ :

$$d\mu_k = \Sigma_k(\partial\mu_k/\partial c_\ell)dc_\ell - s_k dT + \upsilon_k dp, \tag{16.3.3}$$

gives that at $p, T = \text{const}$ the concentration relationship of the diffusive potential coincides with the similar relationship of the chemical potential, $d\zeta_k = d\mu_k$, since $\underline{s}_{ko} = \underline{s}_{ko}(p,T)$:

$$[d\zeta_k]_{p,T} = [d\mu_k\,]_{p,T} = \Sigma_k \, \mu_{k\ell} \, dc_\ell\,, \tag{16.3.4}$$

where $\mu_{k\ell}$ – abridged symbol for the derivative $\partial\mu_k/\partial c_\ell$. Due to this in the general case:

$$d\zeta_k = d\zeta_k = \Sigma_k \mu_{k\ell} dc_\ell - (s_k - s_{ko})dT + \upsilon_k dp \, . \qquad (18.3.5)$$

From here the extended expression of resultant diffusion motive force ensues:

$$\mathbf{F}_k = -[\Sigma_k \mu_{k\ell}\nabla c_\ell + (s_k - s_{ko})\nabla T - \upsilon_k \nabla p] \, . \qquad (16.3.6)$$

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:

$$\mathbf{J}_k = K_k [\Sigma_k \mu_{k\ell}\nabla c_\ell + (s_{ko} - s_k)\nabla T + \upsilon_k \nabla p] \, . \qquad (16.3.7)$$

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 (16.3.7):

$$(\nabla c_k/\nabla T)_{\text{ст}} = -q_k^*/T\mu_{kk} \, , \qquad (18.3.8)$$

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:

$$(\nabla T/\nabla c_k)_{st} = -T\mu_{kk}/q_k^* \qquad (18.3.9)$$

characterizes the stationary Dufour effect (temperature difference arising as a result of component diffusion).

Similarly from (16.3.6) 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 (16.3.6). In this case $\nabla c_k = 0$, and due to mutual compensation of the last two terms it follows that

$$(\nabla p/\nabla T)_{st} = - q_k^*/T\upsilon. \qquad (16.3.10)$$

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) $s_{k\text{o}}$. 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 $s_{k\text{o}}$ 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 (16.3.6) are mutually compensated at $\nabla T = 0$, which directly gives the stationary effect expressed as:

$$(\nabla c_k/\nabla p)_{\text{st}} = -\upsilon_k / \mu_{kk}\,. \qquad (16.3.11)$$

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 (18.2.6) type.

16.4. Simplification of Phenomenological Transfer Laws by Finding Their "Diagonal Form"

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 (5.3.1) and (5.3.2) 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) (5.1.6) for particular processes under investigation. These equations are then considered jointly with Onsager's symmetry conditions (5.1.7) or (5.1.8) 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” (18.1.5) 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:

$$\mathbf{j}_i = -\Sigma_j L_{ij} \nabla\mu_j\,,\ (i, j = 1, 2, \ldots, K\text{–}1). \qquad (16.4.1)$$

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:

$$d\mu_j = \Sigma_k (\partial\mu_j/\partial c_k)dc_k = \Sigma_k \mu_{jk}\, dc_k\,, \qquad (16.4.2)$$

where μ_{jk} – abridged symbol for the derivative $\partial\mu_j/\partial c_k$. Therefore equation (16.4.1) has actually the form:

$$\mathbf{j}_i = -\Sigma_j L_{ij} \Sigma_k \mu_{jk} \nabla c_k\,,\ (i, j, k = 1, 2, \ldots, K\text{–}1) \qquad (16.4.3)$$

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

$$\mathbf{j}_i = -\,\Sigma_j D'_{ik} \nabla c_k\,,\ (i, j, k = 1, 2, \ldots, K\text{–}1) \qquad (16.4.4)$$

by introducing the diffusion coefficients

$$D'_{ik} = \Sigma_k L_{ij} \mu_{jk} \tag{16.4.5}$$

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 (18.4.3) 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 (16.4.3) are most often neglected and the so-called Birchenall-Mehl approximation is used:

$$\mathbf{j}_i = -\,(L_{ij} R_\mu T/a_i)\,\nabla a_i = -\,D_i^*\nabla a_i\,, \tag{16.4.6}$$

or Darken approximation

$$\mathbf{j}_i = -\,D_i^*(\partial a_i/\partial c_i)\nabla c_i = -\,D_i\nabla c_i\,, \tag{16.4.7}$$

wherein the chemical potential $\mu_i = \mu_i^o + R_\mu T \ln a_i$ is represented by a known way in terms of its standard value μ_k^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 (16.4.6) and (16.4.7) 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.16.1). 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.16.1, 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.

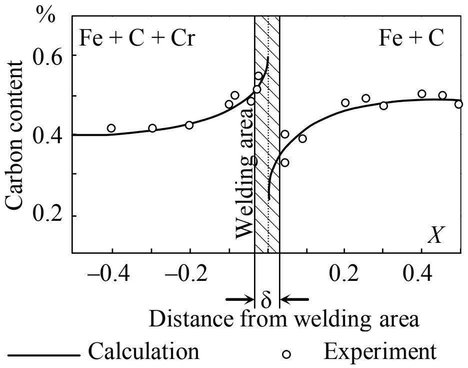

Fig.16.1. Carbon Ascending Diffusion in Alloys

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 (18.3.5) the negative gradient of the diffusion potential ζ_k is the resultant force of the process. However, since $\zeta_k = \mu_k + \mathrm{T}s_{ko} - pv_{ko}$, then at p,T = const the diffusion and the chemical potentials have the same dependence on concentration because $[\mathrm{d}\zeta_k]_{p,T} = [\mathrm{d}\mu_k]_{p,T}$. 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:

$$\mathbf{j}_i = -L_{ii}\Sigma_k\,\mu_{ik}\nabla c_k = -\Sigma_k\,D_{ik}\nabla c_k, \tag{16.4.8}$$

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:

$$D_{ii}/\mu_{ii} = D_{ik}/\mu_{ik} . \qquad (16.4.9)$$

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.16.1), 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 $\mathbf{X}_D{}^c = -\Delta\mu_k = \Sigma_\mathrm{k}\,\bar{\mu}_{ik}\,\Delta c_k$, where $\bar{\mu}_\mathrm{ik}$ – mean value of the coefficient μ_{ik}. Then from expression (16.4.9) it may be found:

$$\Sigma_k\,\bar{\mu}_{ik}\,\Delta c_k = 0 . \qquad (16.4.10)$$

In the particular case of three-component systems with the third component slowly moving:

$$\bar{D}_{23} = \bar{D}_{22}\ (c_2{}' - c_2{}'')/(\mathrm{c}_3{}'' - \mathrm{c}_3{}') , \qquad (16.4.11)$$

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:

$$\Delta\mu_i = -\,\Sigma_k\,\bar{\mu}_{ik}\,\Delta c_k . \qquad (18.4.12)$$

When comparing (18.4.12) with the similar expression $\Delta\mu_i = -\,\bar{\mu}_{ik}\,\Delta c_i$ for a binary system and using relationship (18.4.9) 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:

$$æ_i = 1 + \Sigma_k\,\chi_{ik}\,c_k , \qquad (18.4.13)$$

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 (18.1).

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 (16.4.11) 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.16.1 (Krishtal, 1972).

Table 16.1

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

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 (16.4.10). The calculation and experimental data is shown in Table 16.2.

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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 (18.4.11). 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 Onsager's postulate should be superseded for such processes by a statement each flow depends on only all components of the resultant thermodynamic force.

Table 16.2

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

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 (18.4.2) 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.

16.5. Investigation of Superposition Effects with 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 (16.1.6), 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.16.2).

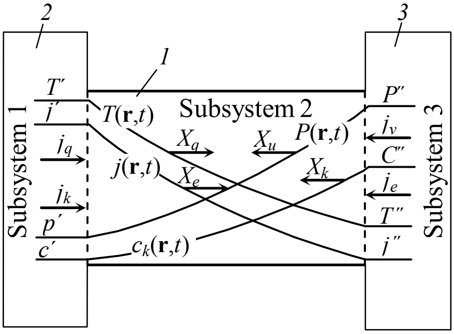

Fig.16.2. Combined (Discontinuous-Continuous) System

1 – membrane (continuum)

2, 3 – reservoirs of heat and substance

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.).

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, $F_{kT} = (s_{k\text{o}} - s_k)\Delta T$ and $F_{kp} = -\upsilon_k \Delta p$, mutually balanced. From here, given the relationship $(s_{k\text{o}} - s_k) = q_k^*/T$ (where q_k^* – the so-called transfer heat of the k^{th} component), a known expression of Feddersen stationary effect directly follows (Groot, 1956):

$$(\Delta p/\Delta T)_{\text{st}} = -q_k^*/T\upsilon_k \,. \qquad (16.5.1)$$

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 ($s_{k\text{o}} = 0$) expression (16.5.1) becomes:

$$(\Delta p/\Delta T)_{\text{st}} = s_k/\upsilon_k \,, \qquad (16.5.2)$$

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:

$$(\Delta c_k/\Delta p)_{\text{st}} = -\upsilon_k/\mu_{kk} \,. \qquad (16.5.3)$$

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:

$$\mathbf{J}_1 = -L_1\,[\Sigma_k \mu_{11}\Delta c_1 + (s_1 - s_{10})\,\Delta T + \upsilon_1\,\Delta p]\,; \qquad (16.5.4)$$

$$\mathbf{J}_2 = -L_2\,[\Sigma_k \mu_{21}\Delta c_1 + (s_2 - s_{20})\,\Delta T + \upsilon_2\,\Delta p]\,. \qquad (16.5.5)$$

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 (16.5.4)…(16.5.5) for the Δc_1 and ΔT the expression of stationary thermo-effusive effect may be found:

$$(\Delta c_1/\Delta T)_{\text{ст}} = (\upsilon_1 q_2^* - \upsilon_2 q_1^*)/T\upsilon\mu_{11}\,. \qquad (16.5.6)$$

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):

$$(\Delta p/\Delta T)_{\text{st}} = -(c_1\, q_1^* + c_2\, q_2^*)/\upsilon\,, \qquad (16.5.7)$$

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 17

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.

17.1. Differential Reciprocal Relations Confirmed in Exponential 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:

$$v_r = \omega_r' - \omega_r'' = \omega_r' \,(1 - \omega_r''/\omega_r') \,. \qquad (17.1.1)$$

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

$$A_r = R_\mu T \ln (\omega_r''/\omega_r') \,, \qquad (17.1.2)$$

where R_μ – universal gas constant.

Considering (17.1.1) and (17.1.2) jointly the kinetic laws of chemical reactions may become exponential dependences of the type:

$$v_r = \omega_r' \,[1 - \exp(-A_r/R_\mu T)] \,. \qquad (17.1.3)$$

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:

$$\omega_r = \omega_{ro} \exp\left(-E_a/RT\right), \qquad (17.1.4)$$

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 (5.5.3) 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 (19.1.3). 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):

$$L \leftrightarrow M \text{ (реакция1)}, \qquad (17.1.5\text{ а})$$

$$M \leftrightarrow N \text{ (реакция 2)}, \qquad (17.1.5\text{ б})$$

or as a linear-dependent elementary reaction model (see Fig.15.

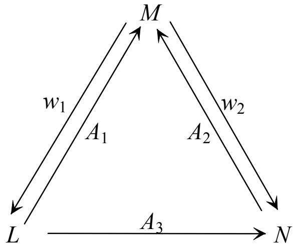

Fig. 17.1. Ternary unimolecular reaction

$$\begin{aligned} &L \leftrightarrow M && \text{(reaction 1)},\\ &M \leftrightarrow N && \text{(reaction 2)}, \qquad (17.1.6)\\ &N \leftrightarrow L && \text{(reaction 3)}. \end{aligned}$$

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

$$v_1 = \omega_1' \left[1 - \exp(-A_1/R_\mu T)\right];$$

$$v_2 = \omega_2' \left[1 - \exp(-A_2/R_\mu T)\right]; \qquad (17.1.7)$$

$$v_3 = \omega_3' \left[1 - \exp(-A_3/R_\mu T)\right],$$

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:

$$T\sigma_s = v_1 A_1 + v_2 A_2 + v_3 A_3 . \qquad (17.1.8)$$

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:

$$v_\alpha = v_1 + v_2 ; \; v_\beta = v_2 + v_3 . \qquad (17.1.9)$$

Two independent forces A_α and $A_\beta$correspond to these rates, which allows equations (19.1.7) to be transformed, subject to the invariance of the dissipation function $T\sigma_s$, to the form:

$$v_\alpha = L_{11} \left[1 - \exp(-A_\alpha/R_\mu T)\right] + L_{12} \left[1 - \exp(-A_\beta/R_\mu T)\right], \qquad (17.1.10)$$

$$v_\beta = L_{21} \left[1 - \exp(-A_\alpha/R_\mu T)\right] + L_{22} \left[1 - \exp(-A_\beta/R_\mu T)\right]. \qquad (17.1.11)$$

Here

$$L_{11} = \omega_1' + \omega_2'; \; L_{12} = \omega_3' \exp(-A_\alpha/R_\mu T)] ; \qquad (17.1.12)$$

$$L_{21} = \omega_3' \exp(-A_\beta/R_\mu T)]; \;\; L_{22} = \omega_1' + \omega_3' . \qquad (17.1.13)$$

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 (17.1.2) 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:

$$\partial v_\alpha / \partial A_\beta = \partial v_\beta / \partial A_\alpha . \qquad (17.1.14)$$

To make sure they are valid, it is enough to differentiate expression (17.1.10) with respect to A_β, given L_{11} and L_{12} independent on A_β, and to repeat the similar operation on (17.1.11) with respect to v_β. The result will be as follows (V. Etkin, 1982):

$$\partial v_\alpha/\partial A_\beta = \partial v_\beta/\partial A_\alpha = (\omega_3'/R_\mu T)\exp(-A_3/R_\mu T). \tag{17.1.15}$$

It can be easily seen that with approaching equilibrium, when A_1, A_2 and A_3 are simultaneously tending to zero, relationship (17.1.15) goes over into known Onsager's symmetry conditions for chemical reactions in the form:

$$L_{12} = L_{21} = \omega_3'/R_\mu T. \tag{17.1.16}$$

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.

17.2. 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:

$$\mathbf{j}_D = -L_{DD}\nabla x_1 - L_{DP}\nabla p\ , \tag{17.2.1}$$

$$\mathbf{j}_V = -L_{PD}\nabla x_1 - L_{PP}\nabla p\ , \tag{17.2.2}$$

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.

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[1] To ascertain those conditions was the main task of the investigation mentioned.

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 said "dusted gas" model certainly comprised the Onsager's symmetry conditions and provided explicit equations for diffusivity and filterability:

$$L_{DD} = (D_1/n_1\gamma_1 + D_2/n_2\gamma_2)/p(n_1\gamma_1 + n_2\gamma_2)\,, \qquad (17.2.3)$$

$$L_{PD} = L_{DP} = (D_1 - D_2)/p(n_1\gamma_1 + n_2\gamma_2)\,, \qquad (17.2.4)$$

$$L_{PP} = (n_1 D_1 + n_2 D_2)/p(n_1\gamma_1 + n_2\gamma_2) + B_o/\nu\,. \qquad (17.2.5)$$

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.

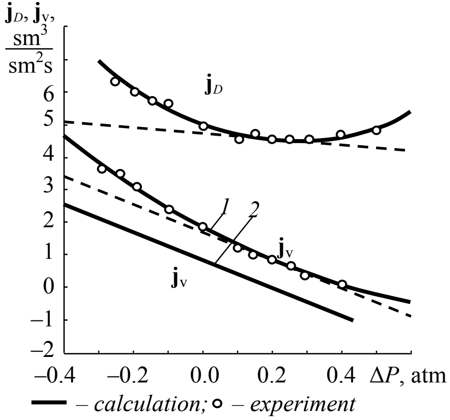
The said dependence of the factors L_{ij} in relationships (17.2.3)-(17.2.5) on the local pressure p and the molar concentrations n_1 and n_2 of the components on the membrane made the diffusion and filtration integral laws

$$\mathbf{j}_D = -L_{DD}^{\mathrm{cp}}\,\Delta x_1 - L_{DP}^{\mathrm{cp}}\,\Delta p\,, \qquad (17.2.6)$$

$$\mathbf{j}_V = -\mathrm{L}_{PD}^{\mathrm{cp}}\,\Delta x_1 - \mathrm{L}_{PP}^{\mathrm{cp}}\,\Delta p \qquad (17.2.7)$$

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.17.2 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 $\mathrm{L_{PD}}$ change much less in value and does not change the sign at all. Only close to the point $\Delta p = 0.2$ 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 (17.2.6)-(17.2.7) 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 $\Delta p > 0.2$ 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 – $\Delta x_{Ar} = 0.963$; 2 – $\Delta x_{Ar} = 0$.

Fig.17.2. 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 (17.3.4)

$$\mathbf{X}_D = -\nabla\zeta_{k1} = -\nabla\mu_1, \tag{17.2.8}$$

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

$$\mu_i = \mu_i^o + R_\mu T \ln p_i . \tag{17.2.9}$$

Applying the ideal gas equation $p_i = px_i = n_i R_\mu T$ (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:

$$\mathbf{X}_D = R_{DD}\,\mathbf{j}_D + R_{DP}\,\mathbf{j}_V \tag{17.2.10}$$

$$\mathbf{X}_V = R_{PD}\,\mathbf{j}_D + R_{PP}\,\mathbf{j}_V \tag{17.2.11}$$

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 19.2.3-19.2.5**.** 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 (19.2.3) and (19.2.4) 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:

$$\bar{\mathbf{X}}_D = \check{R}_{DD}\,\mathbf{j}_D + \check{R}_{DP}\,\mathbf{j}_V \tag{17.2.12}$$

$$\bar{\mathbf{X}}_V = \check{R}_{PD}\,\mathbf{j}_D + \check{R}_{PP}\,\mathbf{j}_V \tag{17.2.13}$$

These laws differ from (19.2.6), (19.2.7) 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 (5.5.3) for such processes. The computation results based on (17.2.3)-(17.2.5) for the same experimental conditions are described in Table 17.1 (V. Etkin, 1983).

Table 17.1

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, $cm^3/cm^2 \cdot s \cdot atm$	
$\bar{X}_D$	$\bar{X}_V$	$\partial j_D/\partial \bar{X}_V$	$\partial \boldsymbol{j}_V/\partial \bar{X}_D$	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

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). 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 17.1 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.

17.3. 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:

$$N^d = \Sigma_i \,|\mathbf{X}_i| \cdot |\mathbf{j}_i| \cos\gamma_i , \qquad (17.3.1)$$

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 $\mathbf{j}_\mathrm{s}$:

$$\mathbf{j}_e = \sigma_\mathrm{e} \mathbf{X}_e^a \cos\gamma_\mathrm{e} = L_\mathrm{e}(\mathbf{X}_e^a)\, \mathbf{X}_e^a , \qquad (19.3.2)$$

$$\mathbf{j}_s = (\lambda/T)\mathbf{X}_q^a \cos\gamma_q = L_q(\mathbf{X}_q^a)\mathbf{X}_q^a , \qquad (19.3.3)$$

where λ, σ_e – thermal conductivity and electric conductivity, respectively, in the absence of magnetic field; $\mathrm{L}_\mathrm{q}(\mathbf{X}_q^a) = \lambda\cos\gamma_\mathrm{q}/\mathrm{T}$; $\mathrm{L}_\mathrm{e}(\mathbf{X}_e^a) = \sigma_\mathrm{e}\cos\gamma_\mathrm{e}$ – phenomenological coefficients as functions of the thermodynamic forces $\mathbf{X}_\mathrm{s}^\mathrm{a}$ 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:

$$X_k = -\left[\Sigma_k \mu_{k\ell}\nabla c_\ell + (s_k - s_{k\mathrm{o}})\nabla T - (\upsilon_k - \upsilon_{k\mathrm{o}})\nabla p + \vartheta_{\mathrm{e}k}\nabla\varphi\right]. \tag{17.3.4}$$

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:

$$\mathbf{j}_k = -L_{kk}\left[\vartheta_{\mathrm{e}k}\nabla\varphi + (s_k - s_{k\mathrm{o}})\nabla T\right]. \tag{17.3.5}$$

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 $\mathbf{j}_\mathrm{e} = \vartheta_{ek}\mathbf{j}_k$ and to simultaneously introduce the related force $\mathbf{X}_\mathrm{e}$ 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:

$$\mathbf{j}_e = \sigma_e \mathbf{X}_e = \sigma_e\left[\mathbf{E} + \mathbf{X}_{\mathrm{e}q}\right], \tag{17.3.6}$$

where $\mathbf{E} = -\nabla\varphi$ – electric field; $\mathbf{X}_{\mathrm{e}q} = -s_\mathrm{e}^*\nabla T$ – thermodynamic representation of the so-called “thermomotive force”; $s_\mathrm{e}^* = (s_\mathrm{e} - s_{\mathrm{e}o})$ – specific (per charge unit) electron transport entropy (Haase, 1967); $\sigma_\mathrm{e} = L_{kk}\vartheta_{\mathrm{e}k}{}^2$.

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 $\mathbf{F}_L = \mathbf{v}_\mathrm{e} \times \mathbf{B} = \upsilon_\mathrm{e}\,\mathbf{j}_\mathrm{e} \times \mathbf{B}$ (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 projection on the charge transfer direction is equal to zero. However, this force is exactly responsible for the artificial anisatropy of the primordially isotropic heat and charge conductors since it changes the direction of the anisotropic electrical conduction resultant force $\mathbf{X}_\mathrm{e}^\mathrm{a} = \mathbf{E} + \mathbf{X}_{\mathrm{e}q} + \mathbf{F}_{\text{л}}$. Allowing for the force $\mathbf{F}_{\text{л}}$ the developed form of the Ohm law becomes:

$$\mathbf{j}_\mathrm{e} = -\sigma_\mathrm{e}\,\mathbf{X}_\mathrm{e}^\mathrm{a} = \sigma_\mathrm{e}\left[\nabla\varphi + s_\mathrm{e}^*\nabla T + \mathbf{F}_{\text{л}}.\right]. \tag{17.3.7}$$

To facilitate further computations, the charge flux $\mathbf{j}_e$ is to be reasonably factored into two components, one of which, j_{ex}, is directed the same way as in the absence of anisotropy, whereas the other, j_{ey}, on the contrary, is caused by anisotropy and directed normally to magnetic field (Fig. 17.3).

In this case

$$j_{ex} = -\sigma_e X_e = \sigma_e [\nabla_x \varphi + s_e^* \nabla_x T], \qquad (17.3.8)$$

$$j_{ey} = \sigma_e \cos\gamma_e [\nabla_y \varphi + s_e^* \nabla_y T], \qquad (17.3.9)$$

where $\nabla_y \varphi$, $\nabla_x T$ and $\nabla_y \varphi$, $\nabla_y T$ – electric potential and temperature gradients on the axes x and y, respectively,

$$\cos\gamma_e = 1 - |\mathbf{F}_л| / |\mathbf{X}_e|. \qquad (17.3.10)$$

The ensuing dependence of cos γ_e on the flux j_e makes the anisotropic electrical conduction law (17.3.7), strictly speaking, non-linear. Nevertheless, as shown above, the differential reciprocal relations (5.5.3) are still valid for it, but in the following form:

$$(\partial j_{e\,y} / \partial X_q^a) = (\partial j_s / \partial X_e^a). \qquad (17.3.11)$$

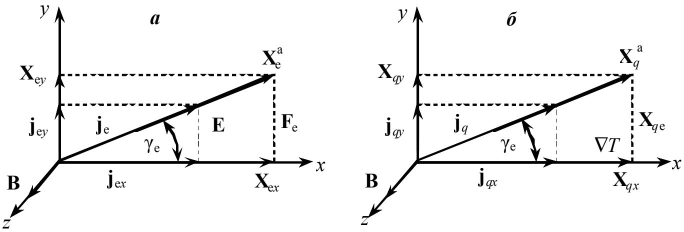


Fig.17.3. Thermal Conductance & Electrical Conductance Anisotropy

These relations allow directly finding the anisotropic thermal conduction. Considering (17.3.9) gives for $\nabla_y \varphi$ being constant:

$$(\partial j_{e\,y} / \partial X_q^a) = \sigma_e X_e (\partial \cos\gamma_e / \partial X_q) = -\sigma_e s_e^*. \qquad (17.3.12)$$

Then according to (17.3.11) considering the components $\mathbf{F}_л$. and $\mathbf{X}_{eq}$ of the force $\mathbf{X}_e^a$ as being constant gives:

$$(\partial j_s / \partial X_e^a) = (\partial j_s / \partial X_e) = -\sigma_e s_e^*. \qquad (17.3.13)$$

This means that in the Fourier law thermodynamic form (5.2.1) generalized to the case of anisotropic thermal conduction an additional term appears $-\sigma_e s_e^* \mathbf{E}$:

$$\mathbf{j}_s = -(\lambda/\mathrm{T})\nabla T - \sigma_e s_e^* \mathbf{E}\,. \qquad (17.3.14)$$

The found diagonal form of equations for anisotropic thermal and electrical conduction allow obtaining all the superposition effects inherent in such systems from the equilibrium conditions, i.e. by the same method as described in the previous chapter.

17.4. 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.19.3), 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'':

$$\sigma_e'' = j_{ex}/\nabla_x \varphi = \sigma_e \cos\gamma_e\,, \qquad (17.4.1)$$

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.17.3) are oriented in the magnetic field direction, i.e. along the axis z ($\mathbf{j}_e = j_{ez}$). Then the angle between the vectors $\mathbf{j}_e$ and **B** is equal to zero, so Ohm's law becomes:

$$j_{ez} = -\sigma_e \cos\gamma_e\, [\nabla_z \varphi + s_e^* \nabla_z T], \qquad (17.4.2)$$

where $\nabla_z \varphi$, $\nabla_z T$ – projections of the vectors $\nabla\varphi$ and ∇T on the current direction.

As follows from this expression, the electric current is a result of the joint action of the thermoelectric force $s_e^* \nabla_z T$ and the electric field $\nabla_z\varphi$. And otherwise, the current flow in the conductor generates a heterogeneous temperature field with the conductor surface releasing (or absorbing) the Thomson heat $q_T^* = Ts_e^*$ 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_T^* it follows that the Thomson effect value is proportional to the current density $\mathbf{j}_e$, 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 (17.3.7). 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 ($j_{ez} = 0$):

$$\alpha_T' = (\nabla_z\varphi/\nabla_z T)_{st} = s_e^*, \tag{17.4.3}$$

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 (19.3.7) $\mathbf{j}_e = j_{ex}; \nabla\varphi = \nabla_x\varphi; \nabla T = \nabla_x T$. For stationary conditions ($j_{e\,x} = 0$) from (17.3.7) the expression for the Thomson cross effect follows as:

$$\alpha_T'' = -(\nabla_x\varphi/\nabla_x T)_{st} = s_e^*. \tag{17.4.4}$$

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

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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.

the angle γ_q with this axis (see Fig. 17.4), the components $\nabla_x T$ and $\nabla_y T$ will be evidently interrelated as:

$$\alpha_{\mathrm{RL}}\,\mathbf{B} = (\nabla_y T/\nabla_x T) = \mathrm{tg}\,\gamma_q\ (\mathbf{j}_{\mathrm{e}} = 0), \tag{19.4.5}$$

where α_{RL} – Righi-Leduc coefficient.

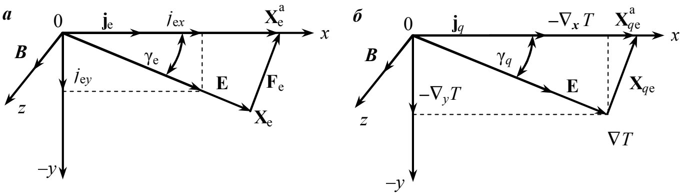

Fig.17.4. Definition of Thermo-Galvano-Magnetic Effects

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 (17.4.4) 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.17.4). Then $\nabla T = \nabla_x T$ and, given the evident relation $\nabla_y\varphi/\nabla_x\varphi = \mathrm{tg}\gamma_e$ (Fig.17.4), the desired relationship can be represented as:

$$\mathrm{A}_{\mathrm{EN}}\mathbf{B} = -\,(\nabla_y\varphi/\nabla_x T) = -\,(\nabla_x\varphi/\nabla_x T)(\nabla_y\varphi/\nabla_x\varphi) = \overset{*}{s}_{\mathrm{e}}\mathrm{tg}\,\gamma_{\mathrm{e}}, \tag{17.4.6}$$

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 $\mathbf{X}_\mathrm{e}$ 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:

$$\alpha_H\mathbf{B} = -(\nabla_y \varphi / j_{ex})_{\text{ст}} = \mathrm{tg}\,\gamma_e/\sigma_e'' \;(j_{ey} = 0), \tag{17.4.7}$$

where α_H – Hall constant.

From (17.4.7) 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 ∇_xT 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 (17.4.5) gives that at this state $j_{sx} = -(\lambda''/T)\nabla_xT + s^*_e j_{ex} = 0$. From this it directly follows that

$$\alpha_N = (\nabla_xT/j_{ex})_{\text{ст}} = Ts^*_e/\lambda'' \;(j_{ey} = 0), \tag{17.4.8}$$

где α_N – Nernst constant; λ'' – thermal conductivity in the transverse magnetic field.

The effect of a temperature gradient of ∇_zT 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 $j_{sz} = -(\lambda/T)\nabla_zT + s^*_e j_{ez}$, so that with the stationary state setting in:

$$\alpha_K = (\nabla_zT/j_{ez})_{\text{ст}} = Ts^*_e/\lambda \quad (j_{ex} = 0), \tag{17.4.9}$$

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 ∇_yT in the direction normal to the current $\mathbf{j}_e = j_{ex}$ and the field **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 (17.4.9) gives instead of $\nabla_x T$:

$$\alpha_\mathrm{E}\,\mathbf{B} = (\nabla_y T\,/j_\mathrm{ex})_\mathrm{st} = T\overset{*}{s}_\mathrm{e}\mathrm{tg}\,\gamma_q/\lambda''\ (j_\mathrm{ey} = 0), \qquad (17.4.10)$$

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.

17.5. 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:

$$T\alpha_\mathrm{EN} = \lambda''\alpha_\mathrm{E}\ . \qquad (17.5.1)$$

This relationship can be also obtained from thermokinetics by comparing expressions (19.4.6) and (19.4.10). Another relationship connects the Nernst effect with the Thomson effect in the transverse magnetic field:

$$\alpha_\mathrm{N} = T\,\alpha_T''/\lambda''. \qquad (17.5.2)$$

This relationship generalizes the thermoelectric effects to the systems in the transverse magnetic fields. It can be also obtained by directly comparing expressions (19.4.9) and (19.4.8). A similar relationship takes place in the longitudinal magnetic field as well:

$$\alpha_\mathrm{K} = T\alpha_\mathrm{T}'/\lambda. \qquad (17.5.3)$$

This expression extends the Thomson relationships obtained for thermocouples to particular current-carrying conductors. It can be also obtained by comparing expressions (17.4.8) and (17.4.14).

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 17.4.8 and 17.4.9), which evidences the identity of the Thomson longitudinal and transverse effects:

$$\alpha_T{}' = \alpha_T{}'' = s_e{}^* \tag{17.5.4}$$

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 17.4.6):

Another relationship, due to $\gamma = \gamma_e = \gamma_q$, connects the Ettinshausen effect (19.4.10) with the Nernst effect (15.4.8):

$$\alpha_N \,\mathrm{tg}\gamma = \alpha_E B \ . \tag{17.5.5}$$

One more relationship connecting the Righi-Leduc and Hall effects can be obtained by comparing expressions (19.4.5) and (19.4.7) given the equality $\gamma_e = \gamma_q$:

$$\alpha_{RL} = \sigma_e{}''\alpha_H \ . \tag{17.5.6}$$

That relationship was earlier set within the electron theory of metals and many times experimentally confirmed.

The relationship between the Righi-Leduc (17.4.5) Ettinshausen-Nernst (17.4.6) effects can be found in the same way:

$$\alpha_{EN} = s_e{}^*\alpha_{RL} \ . \tag{17.5.7}$$

Considering relationships (17.5.6) (17.5.7) jointly gives Wiedemann-Franz law stating constancy of the metal thermal conductance/electric conductance ratio:

$$\Lambda = \lambda''/T\sigma_e{}'' = \alpha_H \,\alpha_{EN}/\alpha_{RL}\,\alpha_E \ , \tag{17.5.8}$$

where Λ is the so-called Lorenz constant. Thus Wiedemann-Franz law, as well as relationship (17.5.6), take a character of the deductions of thermokinetics. This shows, in particular, in the fact that all the above thermomechanical, thermochemical, thermoelectric and thermo-galvanomagnetic 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) deriving them for a particular case of transporting any k^{th} substance in the form:

$$\mathbf{J}_k = K_k \Sigma_i \mathbf{F}_{ki} = L_k \mathbf{X}_k , \qquad (17.5.9)$$

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

$$\mathbf{j}_k = \Sigma_j L_{kj} \mathbf{X}_j . \qquad (17.5.10)$$

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:

$$L_{kk} / \alpha_{kk} = L_{kj} / \alpha_{kj} = L_k . \qquad (17.5.11)$$

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 (17.3.1) 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:

$$L_{kj} / L_{kk} = \mathbf{X}_{kj} / \mathbf{X}_j = \alpha_{kk} / \alpha_{kj} . \qquad (17.5.12)$$

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 (17.5.11) type is evidently equal to (n–1), which gives, with n of such equations, $n(n–1)$ constraints of the (17.5.12) 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 (λ , λ'', σ_e, σ_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.

Conclusion to Part 4

The information set forth in this part is interesting primarily because it states general mechanisms of the substance, charge, momentum and entropy transfer processes in solid, liquid, gaseous media and their unity with the energy transfer processes in force fields.

The new method developed here for description and investigation of phenomena at the interfaces between various scientific disciplines is a further evolution and generalization of the theory of irreversible processes. This shows first of all in extending the applicability of the non-equilibrium thermodynamic methods to states far from equilibrium, wherein processes become nonlinear. The method is distinguishing in not only fundamentally other, hypothesis-free approach to the construction of this theory. It does not exclude from consideration some (reversible or irreversible) part of real phenomena, which allowed exposing the narrowness and groundlessness of the existing linear theory of irreversible processes in the majority of its statements. Among them are the following: Prigogine’s local equilibrium hypothesis, Onsager’s linearity principle, Onsager’s postulate of the generalized rate of some process as depending on all thermodynamic forces in the system, Onsager's interpretation of the reciprocal relations and the "superposition" of irreversible processes in its essence.

Instead, it has been shown that for each independent transfer process an only (resultant) motive force exists which disappearance ceases the process – just as per Fourier, Ohm, Fick, Darcy, Newton, etc laws. The existing therein forces of the same nature being replaced by a resultant of dissimilar forces allowed simplifying the transfer laws, significantly reducing the number of the transfer coefficients to be experimentally defined, removing limitations for their linearity and finding the superposition effects without resorting to the reciprocal relations violated in nonlinear systems. As a major result of such an approach, the concepts have changed as regarding the origin of the flow multiple "superposition" effects. It is shown in the book that all such effects without exception result from the counterdirectivity of the resultant force components and from their equilibrium, but not from the "synergism" (mutual intensification) of their action.

Not less important are the results obtained by applying such an approach to the theory of the field-forms-of-energy transfer. Here not only the unity of transfer processes in substance and field has been determined, but a new explanation for a number of phenomena has been proposed, viz. dependence of acceleration force on velocity, potential retardation phenomenon, reasons of disturbed equilibrium between substance and field, appearing "self-rotation", existing convective components of displacement currents and necessity of their consideration in Maxwell's equations, possibility of single-wire energy transmission and existing longitudinal electromagnetic waves. The consistency of the results obtained has been also demonstrated, as well as the possibility to explain on their basis a number of "anomalies" observed