PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 47, NO. 1, PP. 3–47 (2003)

GOVERNING LAWS OF THERMODYNAMICS

Károly OLÁH

Department of Physical Chemistry
Budapest University of Technology and Economics
H–1521, Budapest, Hungary

Received: October 3, 2003

Abstract

The general laws governing thermodynamic processes and phenomena are recapitulated and completed with new results of kinetic thermodynamics (‘*Thermo-kinetics*’). The treatise consists of three parts. The first one is a recapitulatory of the properties of the fundamental participants of equilibrated macroscopic systems: the densities (C) of the conservative entities (energy, mass) and the set of potentials (F), the equations of state, force laws, cross symmetries, the product-sum of C and F and their differentials. The second part deals with the basic thermodynamic processes, absolute (j) and net fluxes, dynamic force laws, time reversal and cross symmetries, the product-sum of j and F, their various (exact, non-exact, second) differentials. The third part is the story of the inequalities, the ‘arrows’: the Second Law, force arrows and time arrows. The origins of time changes, the evolution toward equilibrium or non-equilibrium steady states. All relations and laws are positioned into a general system of the three basic entities (C, F, j), the three products ($C \cdot F$, $j \cdot F$ and $C \cdot j$), and the three levels of their spatial and/or time-derivatives. Some conventional formulations are modified or generalised. The treatise does not extend over material systems without temperature, nonlinear chemical reactions and instabilities far from equilibrium.

Keywords: thermodynamics, thermokinetics, processes, time-reversibility, reciprocities, evolution.

Introduction

Thermodynamic system is a macroscopic material body having temperature, internal energy and a multitude of microscopic elements (atoms, molecules, electrons, photons, phonons etc.). A number of aspects are known for interpretation and description of thermodynamic systems and laws. There are different viewpoints, applications, aims. Contrary to the classical mechanics, e.g. motion of a single rigid body, the coordinates are fixed here to a given point of place: ‘local’ vs. ‘substantial’ representation. The discussion is ‘material-centered’ (objectivistic) and not ‘man-centered’ (observers, engineers, analysts). In this sense, we will mainly deal with ‘processes’ instead of ‘operations’. We know that the behaviour of the material at a given point depends mainly on its local environment and not on the distance from the wall. We will therefore prefer the ‘local’ vs. ‘global’ treatise (volume element vs. macroscopic system, densities or concentrations vs. macroscopic extensive properties). This treatment proved to be more simple and ‘nature-centered’. As the statements, relations and laws discussed are mainly applied by chemists and physico-chemists, the notations and formulations used here will be familiar for them. The old thermodynamics of the 19. century was a theory of energetics (heat and work). The central problem was to operate the heat engines. Here we strive to get rid of historical, energetic aspects, the classical forms of the ‘Zeroth, First, Second, Third Law’ will be replaced by their generalised and modernised equivalents. We will prefer entropic (e.g., using $1/T$ instead of T) vs. energetic representation, because experiences proved that, doing so, formulisms are more simple and symmetric. And last, we will strive for minimizing the number of postulates.

1. Thermostatics

1.1. The Conservative Properties. The First Law.

The Gibbs State Space

It was Willard Gibbs who laid down the foundation of a systematic theory of macroscopic equilibrium systems [1, 2, 3]. The mean concepts (internal energy, entropy, chemical potential, heat, work, etc.) were introduced and defined under the field of energetics. (‘Energy representation’). The fundamental thermodynamic properties are the variables of the ‘*Gibbs state space*’. The coordinates of this state space are $E_1, E_2, \dots, E_n$, the *independent, extensive, additive, conserved quantities (‘invariants’).*

‘*Extensive*’ means that the property E_i (italic letters) is proportional to the size of the system.

‘*Additive*’ means that if the quantity E_i of two subsystems are $E_i^{(I)}$ and $E_i^{(II)}$, respectively, then for the ensemble of the two subsystems

$$E_i^{(I+II)} = E_i^{(I)} + E_i^{(II)}. \tag{1}$$

‘*Conservativity*’ is of a certain kind of ‘symmetry’. This type of symmetry is formulated by ‘Noether‘s theorem’ which asserts that every continuous symmetry of the dynamical behaviour of a system (i.e., of the dynamical equation and the mechanical potential) implies a conservation law for the system. The symmetry of dynamical laws has important significance under time translation. All fundamental dynamical laws of physics (Newton’s law, Maxwell’s equations and Schrödinger’s equation) are unchanged by the translation $t \rightarrow t + t_0$. If the external potential is independent of time, Noether’s theorem predicts the existence of a conserved quantity, called the *energy*.

The First Law

The first general law expresses the conclusion of the negative experiences of producing energy from nothing: *It is impossible to construct energy producing ‘perpetuum* *mobile'*. The introduction of the concept 'internal energy' has lead to more exact formulations: *The internal energy of an isolated system is constant.* Or for an open system (permeable boundaries): *The flux of the energy* (J_U) *has no production.*

The classical '*First Law*' asserts that the internal energy of a thermodynamic system, similarly to other mechanical energies, is conserved. Up to this point this law is restricted to the energy. Callen [3] has called the attention that thermodynamics is a general, and not only an energetic theory of macroscopic material systems. He proposed a generalization of the First Law extending the conservativity postulate on the momentum and the angular momentum (symmetry under spatial translation and rotation). In most real cases the centre-of-mass of the body is defined as to be in rest, so that the overall momentum and angular momentum disappears. Now a further generalization is needed: extension of the symmetry on other motions such as phase transfers, chemical transformations, in general, transfer from one subsystem into another one. The law can be formulated as follows:

Law of Conservativity

'Conservative' means that if E_i passes from a subsystem (I) into another one (II), then

$$\Delta E_i^{(I)} = +\Delta E_i^{(II)}, \tag{2}$$

no matter if other properties (temperature, pressure, density etc.) of the subsytems are the same or not.

Conservative properties are:

the internal energy (U),
the mole numbers (N_k),
the electric charge,
the overall momentum,
the overall angular momentum,
the volume (V), (or the surface).

At chemical reactions, the mole numbers are not conservative anymore, one has to calculate with atoms instead of molecules. The common property is the lack of 'production'.

$$\frac{\mathrm{d}E_i}{\mathrm{d}t} = -\mathrm{div}\ J_i. \tag{3}$$

Important: only fluxes of conservative quantities have physical meaning. *The independent conservative quantities are the coordinates of the Gibbs state space.*

Carriers, Carried Properties, Charges

A macroscopic body is an ensemble of particles. Let C_z^* be the density of the z'th kind of elementary component (z'th carrier particle). The group of the carrier particles involves more subgroups differing in energy, chemical configuration etc.

Some of the E_i's (e.g., the energy) are bound to particles. The appropriate carried (molar or partial molar) quantities are called the 'charges' (P_{iz}). Such charges are: partial molar energy, molar mass, Faraday-charge etc. In this sense

$$E_i = \sum_z P_{iz} \cdot C_z^*, \tag{4}$$

where: C_z^* is the mole density of the z'th particles.
P_{iz} is the charge of the i'th property carried by a unit of the z'th carrier.

Natural units. In many applications the additive E_i's are placed on the exponent. In this case they must be divided by a 'natural unit'. For the energy the quantity RT is widely used as natural unit, where R is the gas constant ($R = 8.314$ J/K · mol) and T is the absolute temperature. RT is defined as

$$RT \equiv \lim_{P \to 0} (P \cdot V), \tag{5}$$

where P is the pressure and V is the molar volume of an ideal gas. RT has a statistical meaning as well:

$$\frac{1}{RT} = -\frac{\ln x_i - \ln x_k}{E_i - E_k}, \tag{6}$$

where x_i is the fraction of the particles of energy E_i etc. This relation is the integral of

$$-R \cdot \mathrm{d} \ln x = \frac{1}{T} \mathrm{d}E. \tag{7}$$

The natural unit of the volume is the 'characteristic (hyper-) volume' V^* defined as the average cell volume of the configuration phase space

$$V^* = \left(\frac{h_P}{\overline{p}} \right)^s, \tag{8}$$

where h_P is the Planck-constant and $\overline{p}$ is the average ('thermal') momentum and s is the degree of freedom. (At motion of a mass point in a three-dimension space, $s = 3$).

1.2. Entropy and the Third Law

About the physical sense of the quantity called 'entropy' uncertainties prevail up to now. The origins of the obscurity are in the quite different definitions and interpretations in use. What is entropy really? Reduced heat? The measure of disorder? Or the probability? The degree of the lack of information? 'The entropy increases'. What is the background of the increase? The time arrow? Has a system entropy out of equilibrium, or not? Is the entropy really zero at zero absolute temperature? Is the entropy finite when the temperature is infinite or negative? Has a system entropy without temperature? When does exist entropy and when does not at all? Which is the most general definition of the entropy? What is sure, the entropy is closely related to the distributions. The most general definition of entropy, of which all special ‘entropies’ can be deduced is as follows:

If a system is composed of more elements and the set of the elements can be classified into more subsets (fractions), then the (dimensionless) entropy (S) *is*

$$\mathrm{d}S = -\sum_z \ln x_z \cdot \mathrm{d}x_z, \tag{9}$$

where the x_z*’s are the fractions (not probabilities!) of the elements similar (indistinguishable) in one and different (distinguishable) in another respect.*

No requirements are what kind of distinctions are to be made. The elements may differ in energy, chemical character, colour, mass, may be words of different length, people of different mother language and so on. This general entropy can be defined for any (eventually irregular) distribution. In this sense any system has entropy! The entropy is, consequently, optional to some extent. (E.g. the isotopic composition of a given element is to be taken into account only if it undergoes a change. If not, the appropriate entropy-term is superfluous). From this property of entropy results the apparently contradictory statement that entropy always exists (may be defined and calculated) for any kind of regular or irregular distributions.

Thermal entropy: The entropy of the energy-distribution is the ‘thermal’ entropy (S), its dimension is J/K $\cdot$ mol. The natural unit of the thermal entropy is the gas constant (R). The dimensionless entropy S is the thermal entropy divided by the gas constant.

Entropy is an extensive and additive but *non-conservative* quantity. This property results from the fact that the macroscopic entropy is a sum of *products* of invariant extensive quantities (E_i) and ‘intensive’ factors (the potentials, F_i). It can be proved that if all E_i’s are conservative, S cannot be. Because of the ‘non-conservativity’ of S, one cannot speak of an ‘entropy-flux’ (the quantity often called ‘entropy-flux’ is a special product-sum discussed later).

The Third Law

If the entropy of every element in its stable state at $T = 0$ *is taken as zero, every substance has a positive entropy which at* $T = 0$ *may become zero, and does become zero for all perfect crystalline substances, including compounds [4].*

It results from the definition that the Third Law refers only to the ‘thermal’ entropy and thus is a law of limited validity.

1.3. The Potentials. Transitivity. The Zeroth Law

Global System, Energy Representation

In the Gibbsian energetic system the internal energy (U) plays the role of principal quantity and the entropy is one of the extensive coordinates (even if non-conservative).

At local equilibrium U is unique function of the E_i's. The derivative F_i^* is called the i'th ('energetic') potential. An appropriate potential is accompanied to any E_i.

$$F_i = \left(\frac{\partial S}{\partial E_i}\right). \tag{10}$$

The potentials play important roles in thermodynamics: The most important potentials are:

$$\begin{array}{ccc} E_i & & F_i^* \\ \cdots & \cdots & \cdots \\ S & \rightarrow & T \\ N_k & \rightarrow & \mu_k \\ V & \rightarrow & -P, \end{array}$$

where: T is the absolute temperature (K),
μ is the chemical potential (J/mol),
P is the pressure (Pa).

The existence of the potentials infers the existence of equilibrium. For the temperature:

Global equilibrium:	T exists, $\nabla T = 0$;
Local equilibrium:	T exists, $\nabla T \neq 0$ is possible.
Local non-equilibrium:	T does not exist.

Transitivity

If A is in equilibrium with B and B is in equilibrium with C, then A is in equilibrium with C and all (independent) potentials (F_i) equalize,

$$F^*_{A(\mathrm{Eq})} = F^*_{B(\mathrm{Eq})} = F^*_{C(\mathrm{Eq})} \tag{11}$$

In a non-equilibrium state the differences of F^*'s (X) are the '*driving forces*' of the equilibration processes.

$$F_A^* - F_B^* = X_{AB}, \tag{12a}$$
$$F_B^* - F_C^* = X_{BC} \tag{12b}$$

At equilibrium the driving forces (X) vanish.

The transitivity is the consequence of the directed Force- and the Time-arrow (Section 4).

The classical ‘Zeroth Law’ is a statement referring only to the thermal equilibrium.

Zeroth Law

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.
Dependency: If some of E_i’s are associated to each other (e.g. ion and an electric charge, stoichiometry), the set of potentials are to be transformed into an independent one (e.g. the chemical potential is to be added to the molar electric charge: $\mu_e = \mu + z \cdot F$). The transformations are to be carried out under keeping the fundamental balance invariant.

1.4. *The Fundamental Balances*

Gibbs’ space is called the space of state of the E_i’s as ‘coordinates’.

The potentials convert the coordinates into energy. The products of E_i and F_i^* can be terms of a general energy balance. For a global system the balance is:

$$\overbrace{\underbrace{U = T}_{A} \cdot \underbrace{S - P \cdot V}_{\text{Kramers}}}^{H} + \overbrace{\sum_k \mu_k \cdot N_k}^{G} \tag{13}$$

Some partial sums are often used:

The Gibbs free energy:
$$G \equiv \sum_k \mu_k \cdot N_k = H - T \cdot S, \tag{14}$$

The enthalpy:
$$H \equiv U + P \cdot V = G + T \cdot S, \tag{15}$$

The Helmholtz free energy:
$$A \equiv U - T \cdot S = G - P \cdot V, \tag{16}$$

The Kramers-potential:
$$T \cdot S - P \cdot V = G - U, \tag{17}$$

where:

U, V, N_k	are extensive (italic letters), additive and *conservative* quantities,
S, H, A, G	are all extensive and additive but *non-conservative* quantities.
T, P, μ_k	are the potentials (non-additive, non-conservative).

The characteristic variables follow from Legendre transformations.

$$U(S, V, N_k),\ S(U, V, N_k),\ H(S, P, N_k),\ A(T, V, N_k),\ G(T, P, N_k).$$

The so-called Born-square illustrates the relationships (neglecting here N_k’s).

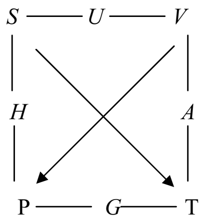


Fig. 1. The Born square

The arrows point at the derivatives (opposite direction: negative).
The differentials are:

GIBBS
$$d\mathbf{U} = T \cdot dS - P \cdot d\mathbf{V} + \sum_k \mu_k \cdot d\mathbf{N}_k, \tag{18}$$

GIBBS–DUHEM
$$0 = S \cdot dT - \mathbf{V} \cdot dP + \sum_k \mathbf{N}_k \cdot d\mu_k, \tag{19}$$

'Second differential'
$$\delta^2\mathbf{U} \equiv dS \cdot dT - d\mathbf{V} \cdot dP + \sum_k d\mathbf{N}_k \cdot d\mu_k > 0. \tag{20}$$

The conservative properties are here underlined to point out that the product sums contain mixed conservative and non-conservative quantities.

Note the asymmetric form of (19) and the positivity of (20).

a. Energy- or entropy representation?

Both disharmonies indicate that the global energy-representation is not the most practical one. The sum can be expressed as function of the energy and the entropy.
Energy representation:
U is the principal, S is the 'thermal' term.
The thermal potential is the temperature.
Entropy representation:
S is the principal, U is the thermal term.
The thermal potential is the reciprocal temperature.

$$dS = (1/T) \cdot d\mathbf{U} + (P/T) \cdot d\mathbf{V} + \sum_k (-\mu_k/T) \cdot d\mathbf{N}_k. \tag{21}$$

Doing so, the sum consists of products including only conservative extensive quantities.

Experiments proved that use of the entropy-representation is more practical in evaluations of temperature-dependence measurements: to make plots of logarithms of vapour pressures (or rate constants or equilibrium constants etc.) vs. $1/T$ (and not T) is advisable. As to the chemical potential, μ is always negative and explicitly temperature-dependent, in contrast to $-\mu/T$ which is positive and less temperature-dependent.

b. Global or local system?

The energy representation is burdened by the *singularity problem:* the number of variables is greater than the number of dimensions of the Gibbs space. In other words, the variables are not all independent, one of them is superfluous. A consequence is that the matrix of the second derivatives of the entropy is singular, its reciprocal cannot be established. The problem is solved by choosing the local system. The '*local system*' is a small area of given fixed volume without any physical walls. The space of state is then spanned by the densities (in other word, the *concentrations*), defined as

$$C_i = \lim_{V \to 0} (E_i/V). \tag{22}$$

By definition, the density of the volume is unity and $\mathrm{d}V \equiv 0$. The superfluous variable, the volume disappears (densities do not depend on the volume). In this way, C_k's form an independent set. Instead of the expansion or contraction $(\mathrm{d}V/\mathrm{d}t)$ the change in the density $(\mathrm{d}C/\mathrm{d}t)$ or the divergency of the flux appears.

The Fundamental Balances in Local Entropy Representation

At local equilibrium the entropy density is a homogeneous function of first order of the densities of the conservative extensive quantities (C_i):

$$\mathrm{d}S = \sum_i F_i \cdot \mathrm{d}C_i, \tag{23}$$

and the derivation leads to another set of potentials (F_i)

$$F_i = \left(\frac{\partial S}{\partial E_i}\right). \tag{24}$$

The two most important potentials are (the entropy density is denoted as S):

$$\begin{array}{ccc} C_i & & F_i \\ \ldots\ldots & \ldots & \ldots\ldots \\ C_U & \rightarrow & 1/T \\ C_k & \rightarrow & -\mu_k/T \end{array}$$

The local versions of the Gibbs and the Gibbs–Duhem relations appear as the differentials of S and $-P/T$, respectively [5]. The sums are full differentials of $\Xi \equiv S - P/T$, the density of the entropic 'Kramers-potential'

$$\Xi = S - P/T. \tag{25}$$

S is a function of the concentrations, and is the principal quantity of the '*density-space*'

$$\mathrm{d}S = (1/T)\cdot \mathrm{d}C_U + \sum_k (-\mu/T)\cdot \mathrm{d}C_k = \sum_i F_i \cdot \mathrm{d}C_i. \tag{26}$$

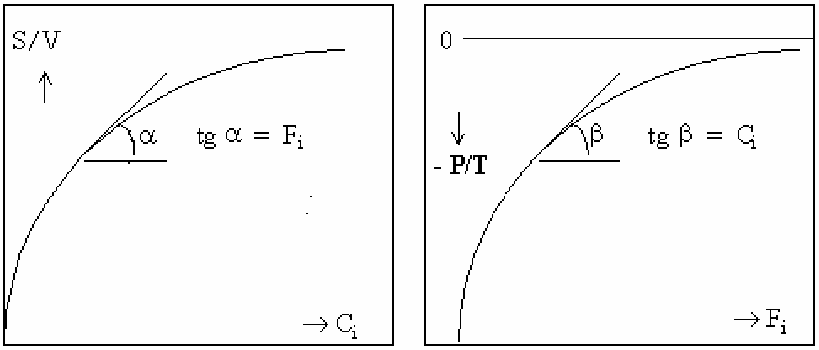
$-P/T$ is a function of the potentials, and is the principal quantity of the '*potential-space*'

$$\mathrm{d}(-P/T) = C_U \cdot \mathrm{d}(1/T) + \sum_k C_k \cdot \mathrm{d}(-\mu_k/T) = \sum_i C_i \cdot \mathrm{d}F_i. \tag{27}$$

$\mathrm{d}(-P/T)$ is the Legendre-transform of $\mathrm{d}S$. The partial derivatives show symmetry

$$F_i = \left(\frac{\partial S}{\partial C_i}\right), \qquad C_i = \left(\frac{\partial\,(-P/T)}{\partial F_i}\right). \tag{28}$$

Remind that for ideal gases $P/T = R \cdot C$ and $\mathrm{d}(P/T) = R \cdot \mathrm{d}C = R \cdot C \cdot \mathrm{d}\ln C$.



(a) Density space (b) Potential space

Fig. 2.

What may mean the differentials 'd'*?* In thermodynamic formulas the differentials are widely used. 'd' is only an abbreviation with several physical meanings. Some of them are:

a. A relatively small change, 'deformation' of the state.
b. Change in space, gradient of a local property (∇C, or ∇F).
c. Change in time: $\mathrm{d}/\mathrm{d}t$.

In the cases b. and c. the fundamental Gibbs-relations refer not only to equilibrium balances but to non-equilibrium and/or non-stationary processes as well.

1.5. The Equations of State (EOS). Cross Symmetry

In local equilibrium the potentials are functions of the densities

$$\mathrm{d}F_i = \sum_k \Gamma_{ik} \cdot \mathrm{d}C_k, \tag{29}$$

and inversely, the densities are functions of the potentials

$$\mathrm{d}C_i = \sum_k \Gamma_{ik}^{-1} \cdot \mathrm{d}F_k, \tag{30}$$

$$\Gamma_{ik} = \left(\frac{\partial F_i}{\partial C_k}\right) \quad \text{and} \quad \Gamma_{ik}^{-1} = \left(\frac{\partial C_i}{\partial F_k}\right). \tag{31}$$

The elements Γ_{ik} form a quadratic matrix (‘*state matrix*’). The diagonal elements $(i = k)$ represent the *self-effects* (e.g. dependence of the internal energy on the temperature). Γ_{ik}’s ($i \neq$k) are responsible for the *cross-effects* between the i’th and the k’th interaction.

Three important properties are worth to study: *Symmetry, Rank, Negativity*.

Cross Symmetry of the State Matrix (Maxwell’s Reciprocity Relations (MRR))

$$\Gamma_{ik} = \Gamma_{ki} \quad (\text{all } i, k). \tag{32}$$

MRR can be proved in several different ways: first, as the symmetry of a second derivative matrix; second, as a transformed diagonal matrix; and third, tested by experiments.

1. Γ_{ik}’s are the elements of the second derivative matrix of the entropy density and Γ_{ik}^{-1}’s are the second derivatives of $-P/T$. It follows from the elementary theorem of calculus that matrix Γ must be symmetric [6]

$$\Gamma_{ik} = \left(\frac{\partial F_i}{\partial C_k}\right) = \left(\frac{\partial^2 S}{\partial C_i \partial C_k}\right) = \left(\frac{\partial^2 S}{\partial C_k \partial C_i}\right) = \left(\frac{\partial F_k}{\partial C_i}\right) = \Gamma_{ki} \tag{33a}$$

$$\Gamma_{ik}^{-1} = \left(\frac{\partial C_i}{\partial F_k}\right) = \left(\frac{\partial^2 (-P/T)}{\partial F_i \partial F_k}\right) = \left(\frac{\partial^2 (-P/T)}{\partial F_k \partial F_i}\right) = \left(\frac{\partial C_k}{\partial F_i}\right) = \Gamma_{ki}^{-1}. \tag{33b}$$

The symmetry may be subject of experimental testing. All observations confirmed that MRR is generally true. As a consequence one may state that: *the existence of the entropy is an experimental fact.*

b. Expressed C_i as carried by the z'th carrier density C_z^*

$$C_i = \sum_z P_{iz} \cdot C_z^*, \tag{34}$$

$$-\mathrm{d} \ln C_z^* = \mathrm{d}F_z^* = \sum_i P_{iz} \cdot \mathrm{d}F_i, \tag{35}$$

$$\begin{aligned} \mathrm{d}C_i &= \sum_z P_{iz} \cdot \mathrm{d}C_z^* + \sum_i C_z^* \cdot \mathrm{d}P_{iz} = \\ &= -\sum_k \left(\sum_z P_{iz} \cdot C_z^* \cdot P_{kz} + \frac{\partial^2 F_z^*}{\partial F_i \partial F_k} \right) \cdot \mathrm{d}F_k. \end{aligned} \tag{36}$$

The expression in the brackets (matrix $\mathbf{\Gamma}$) is invariant against interchanging i and k.

Independence, the rank: If the rank of an $n \times n$ matrix is smaller than n, then the matrix is singular, there is dependence between two rows or columns. In such case the determinant is zero and the reciprocal matrix cannot be calculated.

Energy representation: dependent balance.

Entropy density representation: independent balance.

Summary of Part 1.

Part 1. has dealt with the relationships of the following quantities

C_i	F_i
Conservative property.	Transitivity of potentials.
Generalised *First Law*.	Generalised *Zeroth Law*.
C_z^*	$F_i^* = \ln C_z^*$
Elementary carriers	Elementary potentials

$$C_i = \sum_z P_{iz} . C_z^* \qquad \text{and} \qquad F_i^* = \sum_i P_{iz} . F_i$$

$$d \ln C_z^* = \sum_i P_{iz} . dF_i$$

$$d C_i = \sum_k \Gamma_{ik} . d F_k$$

Maxwell`s cross symmetry relation (MRR):

$$\Gamma_{ik} = \Gamma_{ki}$$

The Kramers-function (Ξ), the entropy-density (S) and - P/T:

$$\sum_i C_i . F_i \equiv$$

$$\equiv \Xi =$$

$$= S + (P/T)$$

The integrals of the non-exact differentials:

$$d S = \sum_i F_i . dC_i \qquad \text{and} \qquad d (P/T) = \sum_i C_i . dF_i$$

2. Processes, Symmetries

2.1. Thermodynamic Processes

Processes and Anti-Processes. Thermokinetics

The thermodynamic system differs from the mechanical one in that, that it consists of a great number of similar elements (particles). Thermodynamic systems are ‘living’ systems in the sense that intensive internal motions take place not only in ‘irreversible’ processes but in equilibrium states as well. Despite all appearances the equilibrium is not a motionless, dead, but a living state, place of a number of intensive internal motions, processes. The word ‘thermo’ means that the system has temperature, the sign of life. Thermodynamic processes are carried by motions or transformations of these elements taking place in space and time. In the kinetic theory ‘Thermokinetics’ the ‘absolute’ process rates play dominant roles [7, 8]. The three fundamental groups of thermodynamic processes are:

a. *Transfers passing a boundary of two (equilibrated) phases:*
   Vaporization/condensation across a liquid-vapor surface.
   Solution/precipitation on a solid/liquid interface.
   Electric charge transfer on a metal/electrolyte interface (‘anodic’ and ‘cathodic’).
   Energy (heat) two-way traffic between two phases.
   Radiative emission/absorption, etc.
b. *Conductive motions inside a phase:*
   Convective or diffusive mass fluxes.
   Heat flow carried by molecules, electrons, phonons, photons.
   Momentum flow.
   Electric conduction carried by electrons or ions.
c. *Scalar processes:*
   Chemical transformations.
   Relaxation processes (restoring the equilibrium structure).

The types of the process rates are:

The product of the surface density and a frequency (moles/m^2 $\cdot$ $1/\mathrm{s}$).
The product of the density and the speed (moles/m^3 $\cdot$ m/s).
The product of a density and a frequency (moles/m^3 $\cdot$ $1/\mathrm{s}$).

2.1.1. *Hierarchy*

The processes can be sorted into three levels of hierarchy.

level 0:	$j^{\rightarrow}$ and $j^{\leftarrow}$	‘Absolute rates’
level I:	$\nabla^2 j$	‘Net rates’ (Onsagerian rates, J)
level II:	$\nabla^2 j$	‘Evolution rates’ (div $J = -\mathrm{d}C/\mathrm{d}t$)

Other known hierarchies are:

level 0:	Point in space;	Location at a moment;	Concentration (C);	Temperature
level I:	Direction;	Velocity;	grad C;	grad T
level II:	Curvature;	Acceleration;	div grad C;	div grad T

Up to the end of the 20th century, only concepts of levels I. and II. are mainly used. However, the zeroth level provides more advantages:

a. Resolution of the net process into time reverse components (‘anti-processes’) makes possible to apply time reverse symmetry laws.
b. Knowing all about the relations of the zeroth level, one knows all the relations of levels I. and II.

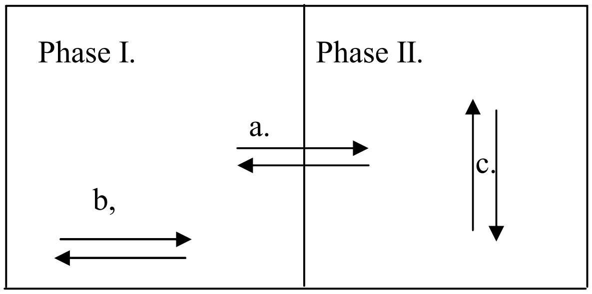


Fig. 3. Time reverse processes

2.2. Time Reversal Invariance of rates

(Transformation $t \rightarrow -t$)

As it is known, all fundamental process rate relationships in mechanics, electrodynamics and quantum mechanics show time reversal symmetry: the equations describing the process rates are invariant under the transformation of $t \rightarrow -t$ and $p \rightarrow -p$ (if a magnetic field is present, $H \rightarrow -H$). The particles of a thermodynamic system all obey the general physical laws and, as it is to be expected, they preserve the time symmetry as well. As it was shown, all the processes listed above have this sort of duality. Any elementary event may take place in two opposite directions. These process pairs are in time-reverse relation with each other. This behavior was put in words by FOWLER (1924) [9]: '*any one process of exchange acting in a particular direction must be invariable companied by an analogous reverse process*'.

EXAMPLES. Evaporation and vapor condensation, the flux of particles of a fluid in directions $+x$ and $-x$, the anodic and cathodic electrode current and chemical reaction 'from left to right' and 'from right to left'.

The Law of Detailed Balance

Paul DIRAC wrote (1924) [10]:

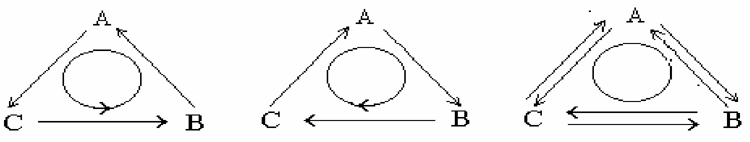
> '*It seems plausible, however, to suppose that all atomic processes are reversible, or, more exactly, that if after any encounter all the velocities are reversed, then the whole process would just repeat itself backwards, the system finally leaving the scene of action being the same as the original systems in the first process and having the reverse velocities. With this assumption, to which there are no known exceptions, each*

> *kind of encounter must be just as likely to occur as its converse in which every velocity has changed sign, the whole process taking place backwards, since there is now perfect symmetry between past and future time.'*

This duality is preserved on the macroscopic level [11, 12].

At equilibrium all reverse macroscopic absolute process rates ($j^{\rightarrow}$ *and* $j^{\leftarrow}$) *equilibrate*, which is equivalent to the statement that: *at equilibrium cycles are not possible*.

$$j_i^{\rightarrow}(\text{eq}) = j_i^{\leftarrow}(\text{eq}) \quad \text{(DB)} \tag{37}$$



Does not occur Does not occur Real case

Fig. 4. Cycles at a triangle reaction

The 'triangular' reaction systems can be used for experimental test.

Observing the changes in the concentrations of B and C after a sudden jump in the concentration of A, a cycle could be detected. The result was [13]: *No traces of equilibrium cycles were found.*

2.3. The Kinetic Mass-Action Law (MA)

The absolute process rate can be formulated as function of the concentrations.

The rate of a process is proportional to the number densities of the participants.

$$j = k \cdot \prod_k C_k^{\nu_k} \tag{38}$$

or

$$\ln j = \ln k + \sum_k \nu_k \cdot \ln C_k. \tag{39}$$

The factor of proportionality (k) is the *rate constant*.

C_k is the molar concentration (number density) of the k'th participant
ν_k is the stoichiometric coefficient of the k'th participant ('charges').

This law is called the 'Mass Action Law' (MA) declared by GULDBERG and WAAGE, 1872, [14]. The law, though it was not declared, was employed since the first half of the 19th century, first of all, for chemical processes. Boltzmann, Maxwell, Einstein, Tolman, Onsager and many others up to now, calculated with rate equations of MA type. The sense of the law seems clear and self-evident. Though, in some instances problems arose. One of them is the kinetic model of the light-matter equilibrium studied by Albert EINSTEIN [15]. Here MA had lead to contradictions. Another example: chemical processes taking place in non-ideal mixtures, where the thermodynamic consistency requires 'activities' instead of concentrations. It has turned out that the problems came from the inconsequent choice of the participants. (Both problems could be solved recently by the author [16, 17]). Further problem arises at chemical processes: the molecules are not conservative. It would be preferable to calculate with the numbers of atoms. Chemical processes would be the topic of another treatise.

The Law of Microscopic Reversibility (MR)

The 'Law of Microscopic Reversibility' declares *the time reverse symmetry of the rate constants.*

$$k^{\rightarrow} = k^{\leftarrow} \tag{40}$$

The name was given by R. T. TOLMAN [18]. TOLMAN's interest was elicited by Einstein's paper dealing with the mass-radiation equilibrium. In 1924 TOLMAN published a paper referring to that of Einstein. Tolman guessed that the equality of two rate constants may be a law of general validity. He wrote: '*This assumption should be recognized as a distinct postulate and might be called the principle of microscopic reversibility*'.

Many years before, BOLTZMANN in his kinetic derivation had used this symmetry successfully [19]. All the same, for many years the notions microscopic reversibility, detailed balance, steady state and equilibrium had been confusing. It is known, however, that at 'macroscopic' processes this law is *not valid* anymore. For example, a chemical reaction

$$A \leftrightarrow B + C \tag{41}$$

$$j^{\rightarrow} = k^{\rightarrow}[A] \quad \text{and} \quad j^{\leftarrow} = k^{\leftarrow}[B]\cdot[C], \tag{42}$$

and

$$k^{\rightarrow} \neq k^{\leftarrow} \tag{43}$$

A question arises: *Is the time reversal symmetry valid only at microscopic processes?*

Some authors suspected that the origin of the violation of MR might be the result of the going over from microscopic to macroscopic, multiparticle system model and looked for a number of elements where the law MR began to be invalid. Others believed that the violation of MR was a sign of the violation of the time reversal symmetry [20]. The truth is that the rate relations chosen (the MA type equations) are not convenient in this sense. The explanation is: the law of MR is valid if the participants are 'ultimate', structureless particles or, their internal structure does not suffer any change during the given process. (The participants may be of macroscopic size as well, e.g. ideal, elastic billiard balls).

2.4. The Charges

Charges are key parts of thermodynamic relations, playing multiple roles. Any process is carried by flow or transfer of elementary carriers (e.g., flux of atoms, molecules, electrons, photons, phonons, other quasiparticles) [21]. The word 'elementary' means that these particles can be regarded structureless mass points or, their internal stucture does not change in the process in question. *Charges connect carriers and carried process rates*.

The absolute flux (transfer, transformation) of the i'th (additive, conservative) quantity is

$$j_i = \sum_i Q_{iz} j_z, \tag{44}$$

where: j_z is the z'th carrier process rate (flux),
j_i is the i'th carried process rate,
Q_{iz} is the i'th quantity carried by a unit carrier flux.

The four most important charges are:

1. The thermal charge (temperature dependent):

$$Q_{\mathrm{th}} = E^* + n \cdot RT, \tag{45}$$

where E^* is the top of the potential energy barrier of the process, and n is the power of the temperature in the 'pre-exponential factor' [22].

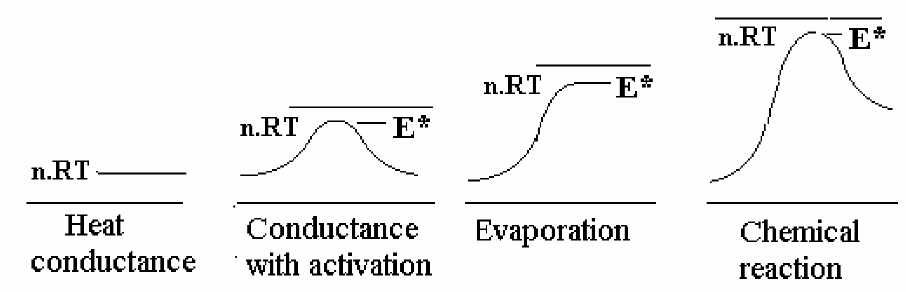


Fig. 5. Versions of the thermal charge

The thermal charge shows exact reverse symmetry:

$$E^{*\rightarrow} = E^{*\leftarrow} \text{ and } n^{\rightarrow} = n^{\leftarrow}. \tag{46}$$

2. The molar momentum (velocity):

$$Q_P = M_k \cdot u, \tag{47}$$

where M is the molar mass, and u is the (average) velocity.

3. The electric charge of a particle (ion) (electric potential):

$$Q_e = z_k \cdot F, \tag{48}$$

where z_k is the number of charge of the k'th ion, and F is the Faraday-charge. (If the particles have electric charges, then the flux of the particles carries electric current).

4. The stoichiometric coefficients ν_{ki} (affinity): The number of the k'th particles as participants in the i'th process. (Caution! Problem at chemical reactions).

Another function of the charges is: *The charges connect carrier and carried potentials:*

$$F_z^* = \sum_i Q_{iz} \cdot \mathrm{d}F_i. \tag{49}$$

The double role of the charges is expressed by a twofold definition:

$$\left(\frac{\partial j_i}{\partial j_z^*}\right) = Q_{zi} = \left(\frac{\partial F_z^*}{\partial F_i}\right). \tag{50}$$

2.5. The 'Potential-Action' (PA) rate equations

PA type rate equations are called relationships where the absolute process rates are expressed in terms of the independent potentials (F_i) [7, 8].

Reciprocal temperature:	$1/T$;
Chemical potential:	$-\mu_k/T$:
Electrochemical potential:	$-(\mu_k + z_k, F)/T$;
Affinity (forward, backward):	$-(\sum_k \nu_k^{\rightarrow} \cdot \mu_k)/T$, $-(\sum_k \nu_k^{\leftarrow} \cdot \mu_k)/T$.

While MA is represented in the configurational space, PA in the potential-space.

This representation exhibits more favourable properties: *Unified, general form of the rate equations.* Analysis of all fundamental physicochemical processes leads to a universal type rate relation. This rate law has the exponential character.

The General Rate Law

$$-R \cdot \mathrm{d}\ln j_z^* = \sum_k Q_{kz} \cdot \mathrm{d}F_k, \tag{51}$$

$$j_i = \sum_z Q_{iz} \cdot j_z^*, \tag{52}$$

Remember that

$$-R \cdot \mathrm{d}\ln j_z^* = \mathrm{d}F_z^* \tag{53}$$

The charges connect process rates and potentials.

The typical integral form of the absolute rate equations for heat/mass transfers is

$$j = j^0 \cdot T^n \exp(-E^*/RT) \cdot \exp(\mu^0/RT) \cdot C^\nu, \tag{54}$$

where the integration constant j^0 is independent of temperature and composition.

Inserting different charges the appropriate process rate relations are resulted.

EXAMPLE. mass and heat transfer.

The thermal potential: $F_1 = 1/T$; the thermal charge: $Q_1 = E^* + n \cdot RT$.
The material potential: $F_2 = -\mu/T$; the material charge: $Q_2 = \nu = 1$ (or, ν_A, ν_B).

The integral form is

$$\int (E^* + n \cdot RT) \cdot \mathrm{d}(1/T) = E^*/T - n \cdot R \cdot \ln T, \tag{55}$$

$$\mu = \mu^0 + RT \cdot \ln C. \tag{56}$$

Table 1.

E^*	n	ν	Absolute process rate	Process
H	n	1	$j = j^0 \cdot T^n$	Heat conduction
H	4	1	$j = j^0 \cdot T^4$	Radiation
H_{vap}	1/2	1	$j = j^0 \cdot T^{1/2} \cdot \exp(-\Delta H_{\mathrm{vap}}/RT)$	Evaporation
H_{vap}	1/2	1	$j = j^0 \cdot T^{1/2} \cdot P/RT$	Vapor condensation
H	n	1	$j = j^0 \cdot T^n \cdot C$	Diffusion (gas)
H_{Diff}	1/2	1	$j = j^0 \cdot T^{1/2} \cdot \exp(-\Delta H_D/RT) \cdot C$	Diffusion (liquid)
H^*	n	ν_A, ν_B	$j = j^0 \cdot T^n \cdot \exp(-\Delta H^*/RT) \cdot C_A \cdot C_B$	Chemical reaction

The General Time Reversal Symmetry (TS)

All rate equations must harmonise with the two equilibrium symmetry laws [23].
The equilibration of the potentials (generalised Zeroth Law):

$$F^{I}_{i\,(\mathrm{Eq})} = F^{II}_{i\,(\mathrm{Eq})}. \tag{57}$$

The equilibration of the absolute fluxes (Law of detailed Balance):

$$j^{\rightarrow}_{(\mathrm{Eq})} = j^{\leftarrow}_{(\mathrm{Eq})}. \tag{58}$$

These requirements demand that, not only at equilibrium, *the rate equations of the time reverse potential-action absolute rates are identical:*

$$j_i^{\rightarrow}(F_k^I) \equiv j_i^{\leftarrow}(F_k^I) \qquad (\text{all } i, k), \quad (\text{RS}) \tag{59}$$

The mathematical forms of the reverse $j(F)$ *rate equations are identical, and all reverse constant parameters (charges) must have the same numerical values*

$$Q_{iz}^{\rightarrow} = Q_{iz}^{\leftarrow}. \tag{60}$$

This is a generalisation of the Law of Microscopic Reversibility, extending the symmetry to all parameters (not only to the rate constant) and over macroscopic rate processes.

EXAMPLE. PA rate equation of evaporation/condensation

Table 2.

Evaporation	Condensation
$j^{\rightarrow}(T) = j^0 \cdot T^{1/2} \exp(-\Delta H_{\text{vap}}/RT)$	$j^{\leftarrow}(T, P) = j^0 \cdot T^{1/2} \cdot P/RT$

Common PA form:

$$j^{\rightarrow}(1/T, -\mu/T) \equiv j^{\leftarrow}(1/T, -\mu/T) =$$
$$= j^0[T^{1/2} \cdot \exp(-E^*/RT)] \cdot \exp(\mu/RT)$$

2.6. *The Dynamic Potential*

The ‘Dynamic Potential’ is defined as the product-sum [24]

$$Z = \sum_i j_i \cdot F_i. \tag{61}$$

Kinetic analogous of the Kramers density Ξ (j_i, instead of C_i)

$$Z = Z_j + Z_F, \tag{62}$$

$$\mathrm{d}Z = \mathrm{d}Z_j + \mathrm{d}Z_F, \tag{63}$$

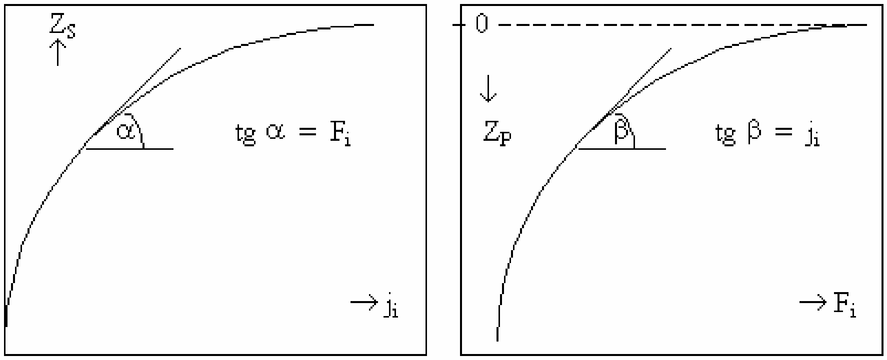
$$\mathrm{d}Z_j \equiv \sum_i F_i \cdot \mathrm{d}j_i; \qquad \mathrm{d}Z_F \equiv \sum_i j_i \cdot \mathrm{d}F_i, \tag{64}$$

$$Z_j \equiv \int \sum_i F_i \cdot \mathrm{d}j_i; \qquad Z_F \equiv \int \sum_i j_i \cdot \mathrm{d}F_i. \tag{65}$$

(Z_j is the analogous of S and Z_F is that of P/T). The derivatives are

$$F_i = \left(\frac{\partial Z_j}{\partial j_i}\right); \qquad j_i = \left(\frac{\partial Z_F}{\partial F_i}\right). \tag{66}$$

As seen, Z_F is a Legendre-transformed of Z_j. As Z_j is the principal dynamic quantity of the kinetic (j) space, Z_F is the same for the potential (F) space.



(a) Z_j in the dynamic space

(b) Z_F in the potential-space

Fig. 6.

2.7. Cross Effects. Reciprocity

The relation between $\mathrm{d}j_i$ and $\mathrm{d}F_i$ can be written formally

$$\mathrm{d}j_i = \sum_k \Lambda_{ik} \cdot \mathrm{d}F_k, \tag{67}$$

where coefficients Λ_{ik} map the process rate-space into the potential-space. In many instances two or more internal processes may interfere with each other. Cross effects represent the interdependence of the i'th flux and the k'th potential: $\Lambda_{ik} \neq 0$ $(i \neq k)$.

The physical origin of a cross effect is found at the *charges*. As told, an appropriate type of charge belongs to any potential (or force field). The i'th force field acts upon j_z^* if and only if $Q_{zi} \neq 0$. For example, the electric potential acts on the motion of a particle if and only if the particle carries electric charge (and, in such case it carries electric current as well). The temperature acts on a process if it carries thermal charge and in turn, this process (flux) carries heat transfer as well. (Example: if the particles have electric charges then the electric field influences their flux). *Cross effect exists if one particle flux carries two or more different charges.*

The relation of j_i and F_k is, supposing first that the Q's are constants:

$$\mathrm{d}j_i = -1/R \cdot \sum_k \left(\sum_z Q_{iz} \cdot j_z^* \cdot Q_{zk} \right) \cdot \mathrm{d}F_k = \sum_k \Lambda_{ik} \cdot \mathrm{d}F_k. \tag{68}$$

Taking into account that Q may depend on some potentials (e.g., the thermal charge is temperature-dependent):

$$\Lambda_{ik} = -1/R \cdot \sum_z j_z^* \cdot \left(Q_{iz} \cdot Q_{kz} + \frac{\partial^2 F_z^*}{\partial F_i \cdot \partial F_k} \right) = \Lambda_{ki}. \tag{69}$$

The sum in the brackets (Λ_{ik}) is *invariant against interchanging i and k*. Cross effects have been discussed by many authors. The earliest of them is due to W. THOMSON on the thermoelectric phenomena [25]. In such cases reciprocities were observed. A good reason to suspect is that the reciprocity may be a general property of processes. If Z_P exists and is a continuous function of the potentials, then Λ_{ik}'s are elements of the second derivative matrix of Z_P. The second derivatives are always symmetrical [5]

The Dynamic Reciprocity Relations (DRR)

$$\Lambda_{ik} = \left(\frac{\partial j_i}{\partial F_k} \right) = \left(\frac{\partial^2 Z_F}{\partial F_i \partial F_k} \right) = \left(\frac{\partial^2 Z_F}{\partial F_k \partial F_i} \right) = \left(\frac{\partial j_k}{\partial F_i} \right) = \Lambda_{ki}, \tag{70a}$$

$$\Lambda_{ik}^{-1} = \left(\frac{\partial F_i}{\partial j_k} \right) = \left(\frac{\partial^2 Z_F}{\partial j_i \partial j_k} \right) = \left(\frac{\partial^2 Z_F}{\partial j_k \partial j_i} \right) = \left(\frac{\partial F_k}{\partial j_i} \right) = \Lambda_{ki}^{-1}. \tag{70b}$$

The Dynamic Reciprocity Relation

$$\Lambda_{ik} = \Lambda_{ki} \qquad \text{(DRR)}. \tag{71}$$

(The dynamic equivalent of MRR). Validity of DRR does not depend on the functional form $j(F)$, consequently, is not confined to linearity. Similarly to the entropy density, second differential elements (Λ_{ik}) may be subjects of experimental checking. Analysis of various known rate equations results that DRR is valid. Consequently, one may declare that *the existence of the dynamic potential is experimentally confirmed.*

2.8. The ‘Irreversible Thermodynamics’. Net process rates

The Onsagerian ‘irreversible thermodynamics’ (IT) has always dealt with ‘net’ fluxes (J_i). (It is a puzzle why absolute rates got quite forgotten in the Onsagerian and post-Onsagerian theories). IT, consequently, has lost any contact with thermostatics.

At non-equilibrium states there appear observable ‘net’ process rates (J) [7, 8].

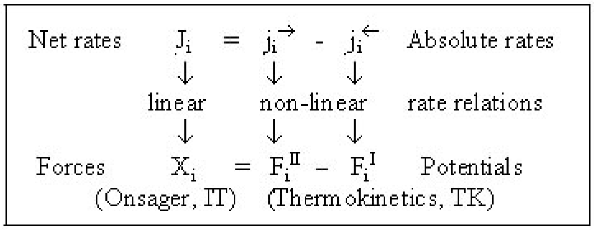
Any ‘net’ process rate (J_i) *is the difference of a ‘forward’* ($j_i^{\rightarrow}$) *and a ‘backward’* ($j_i^{\leftarrow}$) *‘absolute’ process rate:*

$$J_i = j_i^{\rightarrow} - j_i^{\leftarrow} = -\Delta j, \tag{72}$$

or

$$J_i = -\lambda \cdot \nabla j_i. \tag{73}$$

In equilibria net fluxes (and the forces) always vanish, the rate equations degenerate into $0 = 0$. Knowing the rate relations between j_i and F_i, one knows everything about the relations of their differences J_i and X_i. Onsager’s IT forms a part of the kinetic theory as linear limiting case. The differences of the two main process theories can be pictured as follows:



Net rates $J_i = j_i^{\rightarrow} - j_i^{\leftarrow}$ Absolute rates

$\downarrow \quad \downarrow \quad \downarrow$

linear non-linear rate relations

$\downarrow \quad \downarrow \quad \downarrow$

Forces $X_i = F_i^{II} - F_i^{I}$ Potentials

(Onsager, IT) (Thermokinetics, TK)

Table 3. Absolute and net fluxes, potentials and forces, IT and Thermokinetics

Onsager's Reciprocity Relations (ORR)

Lars ONSAGER with his two famous papers (1931, [26]) laid down the foundations of the thermodynamic theory of non-equilibrium ('irreversible') systems. In this work he declared the reciprocity between different processes as a general law.

ONSAGER supposed that, not far from equilibrium, *the (net) fluxes* (J_i) *are linear functions of the forces* (X_k)

$$J_i = \sum_k L_{ik} \cdot X_k, \tag{74}$$

where: J_i is the net rate of the i'th process,
X_k is the k'th thermodynamic driving force, (difference or gradient of the k'th potential)
L_{ik} is the appropriate rate coefficient.

This rate relation can be called the 'Ohm's laws' of thermodynamics.

Onsager's Reciprocity Relations (ORR) express the symmetry of the cross coefficients

$$L_{ik} = L_{ki}. \tag{75}$$

One must stress that L_{ik} can be defined only by the assumed linear relations.

ONSAGER has tried to give a general proof of these relations. His approach was based on the law of 'microscopic reversibility' (declared not long before), supposing that it was a law of general validity responsible for all dynamic symmetries in thermodynamics.

He derived the reciprocities by an argument borrowed from fluctuation theory, with the assumption that the rate at which a fluctuation in an equilibrium ensemble regresses equals the rate at which the ensemble average of the same quantity will change in a nonequilibrium ensemble. For example, he supposed that the average decay of temperature fluctuations obeys the ordinary laws of heat conduction. (His first example was the heat flow in an anisotropic body). He wrote: 'The principle of microscopic reversibility demands that a displacement $\alpha_1 = \alpha_1'$ of energy in the x_1 direction, followed τ seconds later by a displacement $\alpha_2 = \alpha_2''$ by α_1 in the x_2 direction, must occur just as often as $\alpha_2 = \alpha_2''$ followed τ seconds later by $\alpha_1 = \alpha_1'$. Consequently

$$\overline{\alpha_1(t) \cdot \alpha_2(t+\tau) = \alpha_2(t) \cdot \alpha_1(t+\tau)''}. \tag{76}$$

This proof stands, however, on weak grounds. MEIXNER wrote [27] (1973): 'the Onsager-Casimir reciprocal relations yield more information than the fluctuation-dissipation theorem combined with microscopic reversibility'. Onsager was in searching a general proof for the ORR in a difficult position.

First, use of *net* (not *absolute*) fluxes restricted all statements to linear rate relations.

Second, the Microscopic Reversibility concerns only to absolute reverse rates of a *single* process and cannot do anything with cross effect of *different* processes.

Third, the law of Microscopic Reversibility can be applied only to microscopic, atomic processes.

Fourth, in deriving the relations of rate equations Onsager could use only rate equations of $j(C)$ type. As to the heat conductance example of Onsager, another transformation is working here. Taking, namely, the coordinates parallel to the axes of symmetry of the crystal, only three independent heat conductivities (diagonal conductivity matrix) appear.

Transforming the coordinates into another, e.g. a Cartesian system, three transformation parameters are inferred. The number of independent parameters is then $3 + 3 = 6$. But the transformed non-diagonal but symmetrical new matrix consists of $33 = 9$ elements. ORR (matrix $\mathbf{L}$) and DRR (matrix $\mathbf{\Lambda}$) are closely related. Near to equilibrium

$$-\Delta j \approx J = \sum_i L_{ik} \cdot X_k \approx \sum_i L_{ik} \cdot \Delta F_k = -\sum_i \Lambda_{ik} \cdot \Delta F_k. \qquad (77)$$

Consequently, symmetry of Λ is equivalent to the symmetry of L's

$$L_{ik} = -\Lambda_{ik} = -\Lambda_{ki} = L_{ki}. \qquad (78)$$

The difference is that while ORR is restricted to linearity, DRR is of general validity.

Summary of Part 2.

Processes and symmetries

A. *Time reversal symmetries*

Processes are regarded as differences of two time-reverse components

$j^{\rightarrow}$ and $j^{\leftarrow}$

Law of *Microscopic Reversibility* of rate constants of MA rate equations:

MR (Limited validity):

$$k^{\rightarrow} = k^{\leftarrow}$$

Equilibrium symmetry laws of PA rate equations:

Law of *Detailed Balance* The *Law of Transitivity* (Zeroth Law)

DB ZL

$j^{\rightarrow}_{Eq} = j^{\leftarrow}_{Eq}$ $F^{\rightarrow}_{Eq} = F^{\leftarrow}_{Eq}$

The *General Reversal Symmetry Law*

$$j^{\rightarrow}(F^{\rightarrow}) \equiv j^{\leftarrow}(F^{\leftarrow})$$

$$Q^{\rightarrow} = Q^{\leftarrow}$$

The fundamental process rate equations:

$$d \ln j_z^* = d F_z^*$$

$j_i = \sum_z Q_{iz} . j_z^*$ and $d F_z^* = \sum_i Q_{iz} . dF_i$

B. *Cross Symmetries*

The *Dynamic Reciprocity Relations* *Onsager`s Reciprocity Relations*

DRR ORR

$d j_i = \sum_k \Lambda_{ik} . d F_k$ $J_i = \sum_k L_{ik} . X_k$

$\Lambda_{ik} = \Lambda_{ki}$ $L_{ik} = L_{ki}$

(General validity) (Valid only for linear equations)

C. The Dynamic Potential

$$Z \equiv \sum_i j_i . F_i = Z_j + Z_F$$

The (non-exact) differentials:

$d Z_j = \sum_i F_i . d j_i$ and $d Z_F = \sum_i j_i . d F_i$

3. Arrows

3.1. The Second Law

The Second Law declares a negative experience: *It is impossible to construct a perpetuum mobile of second art*.

There is a general property of the material world, the unidirectionality of processes and the 'driving forces':

a. Deformation of the state and the (counter-) force ($\mathrm{d}C \to \mathrm{d}F$).
b. Process rates and forces ($\mathrm{d}j \to \mathrm{d}F$, 'Force arrow').
c. Directed change in time ('Time arrow').

These properties are expressed in mathematical language as inequalities (always negative or always positive) of some thermodynamic quantities. If any of these inequalities ('arrows') would be violated then the Second Law would be invalidated as well. Otherwise, these inequalities express the stability properties of the equations of state (EOS) and the equations of rates (EOR). Unstable states are not forbidden at all but such situations always have a short lifetime.

The introduction of the reverse 'absolute' process rates raises a question: is this type of processes in contradiction with the Second Law or not?

'Unnatural' process rates and the Second Law

The thermal migrations of the particles of a system and the fluxes of the carried conservative properties (flux of heat, momenta, electric charge, etc.) are not strictly unidirected: they are differences of opposite absolute fluxes. The 'naturally' directed fluxes are accompanied by 'unnatural' fluxes. At diffusion, there are molecules migrating towards the greater concentration. There is a part of the heat flow towards the higher temperature. There are anions migrating to the cathode, electrons towards the negative end of a wire and so on. At equilibrium the 'normal' and 'abnormal' processes are equal (50–50 per cent). Contradicts all this the Second Law, or not? The question needs an answer. The answer is satisfying: the Second Law is valid! But the formulation is to be corrected with the dominance of the 'natural' directed processes. *The 'natural' process rates are never less than the 'unnatural' counter-process rates.*

3.2. The Force Arrow

3.2.1. Inequalities

The laws discussed in Sections 1. and 2. were *equalities*. The laws to be studied next are formulated as *inequalities*. This behavior is in close relation with the following properties:

Monotony: The origins of the behaviors below are based on some properties of the EOS (matrix $\mathbf{\Gamma}$) and the EOR (matrix $\mathbf{\Lambda}$). One of them is the monotony.

Stability: Stability means that any deformation of an equilibrated body generates a counter-force. This force drives a counter-process and restores the equilibrium.

Definite state matrices: The thermodynamic system is stable when matrices $\mathbf{\Gamma}$ and $\mathbf{\Lambda}$ are (negative) definite.

The second differentials: The negativity of matrices $\mathbf{\Gamma}$ and $\mathbf{\Lambda}$ is equivalent to the negativity of the second differentials of the appropriate fundamental quantities, e.g., the entropy and the dynamic potential, respectively.

In general, a matrix $\mathbf{A}$ is positive/negative definite if for a system of linear equations

$$\mathbf{y} = \mathbf{A} \cdot \mathbf{x} \tag{79}$$

the scalar product of the vectors $\mathbf{x}$ and $\mathbf{y}$ is always positive (or negative)

$$\mathbf{A} < 0 \quad (\text{or}, > 0) \qquad \text{if} \qquad \mathbf{y} \cdot \mathbf{x} < 0 \quad (\text{or}, > 0). \tag{80}$$

Negativity of the matrix $\mathbf{A}$ and of the scalar product $\mathbf{y} \cdot \mathbf{x}$ means that elements of $\mathbf{y}$ are in monotonous degressive relation with the elements of $\mathbf{x}$.

Definite Matrices:

In the present instances three main matrices are worth of attention.

$$\mathrm{d}C_i = \sum_k \Gamma_{ik} \cdot \mathrm{d}F_k \quad \text{(non-linear)} \quad \text{and matrix} \quad \mathbf{\Gamma} \le 0, \tag{81}$$

$$\mathrm{d}j_i = \sum_k \Lambda_{ik} \cdot \mathrm{d}F_k \quad \text{(non-linear)} \quad \text{and matrix} \quad \mathbf{\Lambda} \le 0, \tag{82}$$

$$\mathrm{d}j_i = \sum_k \Delta_{ik} \cdot \mathrm{d}C_k \quad \text{(linear)} \quad \text{and matrix} \quad \mathbf{\Delta} \le 0, \tag{83}$$

and

$$\mathbf{\Lambda} = \mathbf{\Delta} \cdot \mathbf{\Gamma}. \tag{84}$$

On the language of matrix calculus, for all diagonal minor-matrices of n-order

$$\frac{\mathbf{\Gamma}_n}{\mathbf{\Gamma}_{n-1}} \le 0, \qquad \frac{\mathbf{\Lambda}_n}{\mathbf{\Lambda}_{n-1}} \le 0, \qquad \frac{\mathbf{\Delta}_n}{\mathbf{\Delta}_{n-1}} \ge 0. \tag{85}$$

All diagonal elements of $\boldsymbol{Gamma}$ and $\mathbf{\Lambda}$ (and all minor determinants of even order) are then negative and all minor determinants of $\mathbf{\Delta}$ are positive. Consequently

$$\Gamma_{ii} < 0, \qquad \Lambda_{ii} < 0, \quad \text{and} \quad \Delta_{ii} > 0 \tag{86}$$

and the absolute values of the non-diagonal elements are limited:

$$\Gamma_{12}^2 \leq \Gamma_{11}\Gamma_{22}, \quad \Lambda_{12}^2 \leq \Lambda_{11}\Lambda_{22}, \quad \text{and} \quad \Delta_{12}^2 \leq \Delta_{11}\Delta_{22}. \tag{87}$$

(E.g. the heat capacity, the heat conductance are always positive, the values of expansion coefficient or the thermoelectric coefficient are limited). The geometrical consequence is that the entropy density is convex (negative curvature) in the density space (and $-P/T$ is convex in the potential-space) and the dynamic potential is convex in the process rate space. As told, all these are equivalent to the negativity of the two scalar second differentials (not the second derivatives!). Remember that symbol 'd' can mean (small or great) differences or gradients (∇), or time rates of change $(\mathrm{d}/\mathrm{d}t)$.

One can observe the analogy between Z and Ξ, X and S, Y and $-P/T$, x_i and C_i, y_i and F_i.

The potentials F_i are monotonous decreasing non-linear functions of the C_i's, and the potentials F_i are monotonous decreasing non-linear functions of the j_i's, and j_i's are monotonic increasing linear functions of the C_i's.

Factors Δ_{ik}'s are approximately constants but Γ_{ik}'s and Λ_{ik}'s are not (non-linear).

3.2.2. Exact and Non Exact Differentials

Let be

$$Z(x_i, y_i) = X(x_i) + Y(y_i) \equiv \sum_i y_i \cdot x_i, \tag{88}$$

$$X = \sum_i \int y_i \cdot \mathrm{d}x_i \qquad \text{and} \qquad Y = \sum_i \int x_i \cdot \mathrm{d}y_i, \tag{89}$$

$$\mathrm{d}X = \sum_i y_i \cdot \mathrm{d}x_i \qquad \text{and} \qquad \mathrm{d}Y = \sum_i x_i \cdot \mathrm{d}y_i, \tag{90}$$

$$\mathrm{d}^2X = \sum_i y_i \cdot \mathrm{d}^2x_i \qquad \text{and} \qquad \mathrm{d}^2Y = \sum_i x_i \cdot \mathrm{d}^2y_i \tag{91}$$

If function $y(x)$ is linear then $X = Y = Z/2$
If function $y(x)$ is non-linear then $X \neq Y$.
If a unique function $y(x)$ does not exist then X and Y do not exist as well.
An interesting nonlinear example is:

$$Y_i = \ln x_i. \tag{92}$$

Then

$$Z = X + Y = \sum_i x_i \cdot \ln x_i, \tag{93}$$

$$X = \sum_i x_i \cdot (\ln x_i - 1) \quad \text{and} \quad Y = \sum_i x_i, \tag{94}$$

$$\mathrm{d}X = \sum_i \ln x_i \cdot \mathrm{d}x_i \quad \text{and} \quad \mathrm{d}Y = \sum_i \mathrm{d}x_i. \tag{95}$$

The three fundamental product-sums of thermodynamics are:

$$Y \equiv \sum_i C_i \cdot j_i = Y_C + Y_j, \tag{96}$$

$$\Xi \equiv \sum_i C_i \cdot F_i = \Xi_C + \Xi_F, \tag{97}$$

$$Z \equiv \sum_i j_i \cdot F_i = Z_j + Z_F. \tag{98}$$

The six differentials and their integrals are

$$Y_C \equiv \int \sum_i j_i \cdot \mathrm{d}C_i; \qquad Y_j \equiv \int \sum_i C_i \cdot \mathrm{d}j_i, \tag{99}$$

$$\Xi_C \equiv \int \sum_i F_i \cdot \mathrm{d}C_i; \qquad \Xi_F \equiv \int \sum_i C_i \cdot \mathrm{d}F_i, \tag{100}$$

$$Z_j \equiv \int \sum_i F_i \cdot \mathrm{d}j_i; \qquad Z_F \equiv \int \sum_i j_i \cdot \mathrm{d}F_i. \tag{101}$$

Some of them play important roles in thermodynamic calculations.

$$\Xi_C = S \quad \text{(the entropy density)}, \tag{102}$$

$$\Xi_F = -P/T, \tag{103}$$

if $-\mathrm{d}j_i$ means the net flux (J),

$$\mathrm{d}Z_j = -\sum_i F_i \cdot J_i \tag{104}$$

the ‘entropy flux’.

3.2.3. Second Differentials

The monotonic properties of the EOS and EOR lead to the negativity (or positivity) of the appropriate second differentials (not second derivatives!).

$$\delta^2 Y = \sum_i \mathrm{d}C_i \cdot \mathrm{d}j_i = \sum_i \sum_k \mathrm{d}C_i \cdot \Delta_{ik} \cdot \mathrm{d}C_k \geq 0 \quad \text{(decreasing} \rightarrow \text{minimum)} \tag{105}$$

$$\delta^2 \Xi = \sum_i \mathrm{d}C_i \cdot \mathrm{d}F_i = \sum_i \sum_k \mathrm{d}F_i \cdot \Gamma_{ik}^{-1} \cdot \mathrm{d}F_k \leq 0 \quad \text{(increasing} \rightarrow \text{maximum)} \tag{106}$$

$$\delta^2 Z = \sum_i \mathrm{d}j_i \cdot \mathrm{d}F_i = \sum_i \sum_k \mathrm{d}j_i \cdot \Lambda_{ik}^{-1} \cdot \mathrm{d}j_k \leq 0 \quad \text{(increasing} \rightarrow \text{maximum).} \tag{107}$$

Symbol ‘d’ means spatial (‘∇’) or time change ($\mathrm{d}/\mathrm{d}t$).

The ‘Entropy Flux’

The product of net fluxes and the appropriate potentials ‘Entropy flux’ named:

$$J_S \equiv \sum_i F_i \cdot J_i \qquad (= -\lambda \cdot \nabla Z_j). \tag{108}$$

Exactly, J_S is not a real flux in a strict sense: this product is not a conservative property (contrary to J_i). Exactly, J_S is the change in the entropy due to the transport passing the boundary (‘external entropy change’).The derivatives of J_S are important quantities:

$$\nabla J_S = \sum_i F_i \cdot \nabla J_i + \sum_i J_i \cdot \nabla F_i = -\sum_i F_i \dot{C}_i + \sum_i J_i \cdot X_i = -\dot{S} + P_S. \tag{109}$$

The Entropy Production

The second differential of the kinetic potential, $\delta^2 Z$ has an outstanding importance.

The net fluxes and the forces are

$$\mathrm{d}j_i = \lambda \cdot \nabla j_i = -J_i \quad \text{and} \quad \mathrm{d}F_i = \nabla F_i = X_i, \tag{110}$$

then the inequality

$$\lambda \cdot \delta_\nabla^2 Z \equiv \lambda \cdot \sum_i \nabla j_i \cdot \nabla F_i = -\sum_i J_i \cdot X_i \leq 0 \tag{111}$$

is equivalent to the positivity (and decreasing tendency) of the Entropy Production (P_S)

$$P_S \equiv \sum_i J_i \cdot X_i \geq 0 \qquad (\rightarrow \text{minimum}). \tag{112}$$

The Differentials of the Entropy Production

$$\mathrm{d}P_S = \mathrm{d}_J P_S + \mathrm{d}_X P_S = \sum_i \mathrm{d}J_i \cdot X_i + \sum_i J_i \cdot \mathrm{d}X_i. \tag{113}$$

If

$$J_i = \sum_i L_{ik} \cdot X_k, \tag{114}$$

and L_{ik}'s are constants, then

$$\mathrm{d}_J P_S = \sum_i \sum_k X_i \cdot L_{ik} \mathrm{d}X_k = \sum_i \mathrm{d}_X P_S = \sum_i \sum_k J_i \cdot L_{ik}^{-1} \mathrm{d}J_k = 1/2 \mathrm{d}\, P_S \tag{115}$$

and

$$\int \mathrm{d}_J P_S = \int \mathrm{d}_X P_S = 1/2 P_S \tag{116}$$

(called by PRIGOGINE as 'Dynamic potential' [28, 29]). 'd' may mean operation '∇' or '$\mathrm{d}/\mathrm{d}t$'. For a single process ($i = k = 1$ and $L_{ik} = L$).

$$\mathrm{d}_J P_S = L \cdot \mathrm{d}(X^2) = \mathrm{d}_X P_S = L^{-1} \mathrm{d}(J^2) = 1/2 \mathrm{d}\, P_S. \tag{117}$$

Summing up, the inequalities, expressing the 'force arrow', provide relations between quantities of the same generation, i.e. $j - c$, $\mathrm{d}j - \mathrm{d}c$, $\mathrm{d}^2 j - \mathrm{d}^2 C$ and so on. These relations mark the tendencies toward the appropriate rest states, e.g. equilibrium, homogeneity, steady state. Though the fluxes j, J contain the time as a variable, about the rates of the evolution processes they cannot give enough information.

One can ask another question: '*Does the force drive the process or does the process create the force?*'

Remember that the ultimate elementary relationship has the form:

$$\mathrm{d}F_z^* = -\mathrm{d} \ln j_z^*. \tag{118}$$

It seems that the second statement stands nearer to the reality: the force is not an external stress, it is rather an object of aim. Is then the 'force arrow' a triviality?

3.3. The Time Arrow

Our next task is to analyse the relations between thermodynamic quantities and their changes in time. A number of such relations are known, mostly belonging to the group of the third generation. Examples: Fick's second law, Fourier's 'second' law (time change of the distribution of the concentration or the temperature).

3.3.1. Kinetic Origins of the Time Arrow

The Principle of Dissipation

In this section the rate of the time change will be designed by superscript 'point' ($\dot{S}$).

Balances. Fluxes are transfers of carriers and carried properties from one point (or subsystem, or state) to another. Being this property a conservative additive quantity, *in the process the participants are consumed and the products are produced.*

The direction is evident. A quantitative statement is expressed by the Mass Action law: *any process rate is proportional to the number (density) of the participants.*

As the most simple system consider a body of volume V (m^3) containing N_z moles of (carrier) particles (density: C_z^*) and a single absolute flux j_z^* passing the surface A (m^2)

$$C_z^* \to j_z^*, \tag{119}$$

$$-\dot{N}_Z^* \equiv -V \cdot \dot{C}_Z^* = j_z^* \cdot A. \tag{120}$$

If the flux carries i'th type charge (Q_{iz}), the balance (BA) writes

$$-(V/A)\dot{C}_i = j_i \qquad \text{(BA)} \tag{121}$$

The 'equation of rate' expresses a proportionality between C and j

$$j = \overline{u} \cdot C \qquad \text{(EOR)}, \tag{122}$$

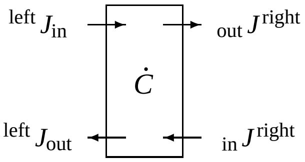
where $\overline{u}$ is the average speed of the particles in the direction of j. From BA and EOR it follows the equation for the time rate of C_i

$$-\dot{C}_i = k \cdot C_i \qquad \text{(MA)}, \tag{123}$$

where k (s^{-1}) is the average frequency of the particles passing the surface and the 'arrow' is represented by the inequality

$$k > 0. \tag{124}$$

Positivities or negativities of time derivatives of some second differentials express trends toward the equilibrium. In a more general, open system

	$\underbrace{{}^{\text{left}}J_{\text{in}} - {}^{\text{left}}J_{\text{out}}} - \underbrace{{}_{\text{out}}J^{\text{right}} - {}_{\text{in}}J^{\text{right}}}$ $\underbrace{{}^{\text{left}}J - {}^{\text{right}}J}$ $\dot{C}$	$\Delta\Delta_j$ $\downarrow$ Δ_j $\downarrow$ $\dot{C}$	div grad$_j$ $\downarrow$ $-\text{div}J$ $\downarrow$ $\dot{C}$

where: ${}^{\text{left}}J_{\text{in}}$ means the input flux from the left side environment,
${}_{\text{out}}J^{\text{right}}$ means the output flux to the right side environment, etc.

In a continuous system the general balance demands (λ is a characteristic length)

$$\dot{C}_i = -\lambda \cdot \nabla^2 j_i. \qquad \text{(BA)} \tag{125}$$

And last,

$$\nabla^2 j_i = \overline{u} \cdot \nabla^2 C_i. \tag{126}$$

In a compressed form

$$-\lambda \cdot \nabla^2 j_i = \dot{C}_i = -(A/V) \cdot j_i = -k \cdot C_i = (\lambda \cdot \overline{u}) \cdot \nabla^2 C_i. \tag{127}$$

Here λ, A, V, k and $\overline{u}$ are all positive.

3.3.2. *The Time Arrow Driven by the Force Arrow*

In the former section only relations of the densities and process rates are studied. In another group of relations the potentials (F_i) play important roles. Some derivatives of product-sums $\sum_i F_i \cdot C_i$ and $\sum_i F_i \cdot j_i$ deserve significant attention.

The time arrow points the direction of the evolution of some second differentials [30].

$$\begin{array}{ccccc}
\sum_i \mathrm{d}j_i \cdot \mathrm{d}C_i & & 0 \;\ldots\ldots\ldots\ldots\; 0 & & 0 \;\ldots\ldots\ldots\ldots\; 0 \\
\downarrow & \text{Time} & \uparrow & \text{arrow} & \uparrow \\
0 \;\ldots\ldots\ldots\ldots\; 0 & & \sum_i \mathrm{d}C_i \cdot \mathrm{d}F_i & & \sum_i \mathrm{d}j_i \cdot \mathrm{d}F_i \\
\text{Decrease} & & \text{Increase} & & \text{Increase}
\end{array}$$

$$\text{a.} \qquad \frac{\mathrm{d}}{\mathrm{d}t}(\delta_{\nabla}^{2}Y) \equiv \frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{i}\nabla j_i \cdot \nabla C_i\right) \geq 0, \tag{128}$$

$$\text{b.} \qquad \frac{\mathrm{d}}{\mathrm{d}t}(\delta_{\nabla}^{2}\Xi) \equiv \frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{i}\nabla C_i \cdot \nabla F_i\right) \geq 0, \tag{129}$$

$$\text{c.} \qquad \frac{\mathrm{d}}{\mathrm{d}t}(\delta_{\nabla}^{2}Z) \equiv \frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{i}\nabla j_i \cdot \nabla F_i\right) \leq 0, \tag{130}$$

and, because $\mathbf{\Gamma} \leq 0$, $\mathbf{\Lambda} \leq 0$, $\Delta \geq 0$,

$$\frac{\mathrm{d}}{\mathrm{d}t}(\nabla j_i)^2 \leq 0, \qquad \frac{\mathrm{d}}{\mathrm{d}t}(\nabla F_i)^2 \leq 0, \qquad \frac{\mathrm{d}}{\mathrm{d}t}(\nabla C_i)^2 \leq 0. \tag{131}$$

a. The $J = -\nabla j$ flux act as smoothing effect on ∇C (→ homogeneity).
b. The trend toward the decrease of the forces (∇F) (→ equilibrium).
c. Time change of the Entropy Production (→ stationary state). In other form

$$\frac{\mathrm{d}_X}{\mathrm{d}t}P_S \leq 0. \tag{132}$$

This inequality was declared by I. PRIGOGINE (1945) [30].

The ‘Fourth’ Differentials

The ‘fourth’ differentials measure the distance from the steady (linear) distribution.

$$\dot{C} = D \cdot \nabla^2 C = \nabla^2 j \qquad \text{(Fick II.)} \tag{133}$$

$$D \cdot (\nabla^2 C)(\nabla^2 j) = (\nabla^2 j)^2 \geq 0. \tag{134}$$

Smoothing of the curvature of the concentration distribution.

3.3.3. The Production of the Entropy

From the time of Clausius up to now, the increase of the entropy (in an isolated system, in absence of any outer supply!) is thought to be a unique phenomenon in nature being of general validity. Clausius said: ‘The entropy of the Universe is increasing’. A lot of questions are to be answered. What is really the entropy increase? Does the asymmetry of the time (‘time arrow’) appear here? Is it the measure of the ‘irreversibility’? Is it equivalent to the Second Law? Is the ‘production of entropy’ identical with the ‘Entropy Production’ function? Is it a unique phenomenon or occur other entities having similar property as well? Cannot entropy decrease? Many answers are given, but no one of them represents the full truth. The entropy does not increase when the densities are constant in time, e.g. at equilibrium and in a steady (but, may be, 'irreversible') open system as well. In the latter case, as we will see, the 'entropy production' does not vanish. What is known:

a. The increase of entropy takes place only in special conditions (isolated system).
b. Other conditions lead to 'time-directed' change of other quantities.

Recapitulating some relations and definitions.

$$\dot{C}_i = -\mathrm{div}\,\mathbf{J}_i = \lambda \cdot \mathrm{div}\,\mathrm{grad}\, j_i = \lambda \cdot \nabla^2 j_i. \tag{135}$$

Three entities are worth mentioning:

a. The time change of the entropy density (may be positive or negative):

$$\dot{S} = \frac{1}{\lambda} \cdot \nabla^2 Z_j = \sum_i F_i \cdot \nabla^2 j_i = \sum_i F_i \cdot \dot{C}_i. \tag{136}$$

b. The Entropy Production (always non-negative) [31]–[33]:

$$P_S = -\lambda \cdot \sum_i \nabla F_i \cdot \nabla j_i = \sum_l J_i \cdot X_i \geq 0. \tag{137}$$

c. The 'entropy flux' (may be positive or negative):

$$J_S = -\lambda \nabla Z_j = -\lambda \cdot \sum_i F_i \cdot \nabla j_i = \sum_i F_i \cdot J_i. \tag{138}$$

Illustration. Let us see three simple system models.

a. A closed system consisting of two parts with potentials F^I and F^{II}, respectively. Let be a flux of a conservative quantity directed from I to II. Let the volumes be unity.
The balance of the flux and the time change of the entropy change can be formulated.
The production of entropy is here equal to the non-negative 'Entropy Production'.

$$-\dot{C}_i^I = J_i = \dot{C}_i^{II}$$
$$F_i^I \dot{C}_i^I + F_i^{II} \dot{C}_i^{II} = (F_i^I - F_i^{II}) J_i = X_i J_i \geq 0$$
$$\dot{S} = \sum_i X_i J_i = P_S \geq 0$$

$$\dot{C}_i = \sum_k \Gamma_{ik} \dot{F}_k$$

$$-\sum_k \Gamma_{ik} \dot{F}_k^I = J_i = \sum_k \Gamma_{ik} \dot{F}_k^{II}$$

$$2J_i = \sum_k \Gamma_{ik} \dot{X}_k$$

$$\frac{\mathrm{d}_X}{\mathrm{d}t} P_S = J_i \dot{X}_i \leq 0$$

Because matrix of Γ_{ik} is negative, *in a closed system the entropy increases,* ‘$\mathrm{d}_X P_S$’ *is negative,* P_S *decreases* (Prigogine’s ‘General Evolution Criterion’).

b. Open system The fluxes passing the outer walls of I and II be J^I_{ext} and J^{II}_{ext}. Here, the production of entropy and the Entropy Production are not the same. Neither $\mathrm{d}S/\mathrm{d}t$, nor $\mathrm{d}_X P_S/\mathrm{d}t$ are definite (positive and negative, respectively). The balances are

$$-\dot{C}^I = J + J^I_{\text{Ext}} \qquad \text{and} \qquad \dot{C}^{II} = J + J^{II}_{\text{Ext}}$$

$$F^I \cdot \dot{C}^I + F^{II} \dot{C}^{II} = X \cdot J + (F^I \cdot J^I_{\text{Ext}} - F^{II} \cdot J^{II}_{\text{Ext}})$$

$$\dot{S} = P_S - \Delta J_S.$$

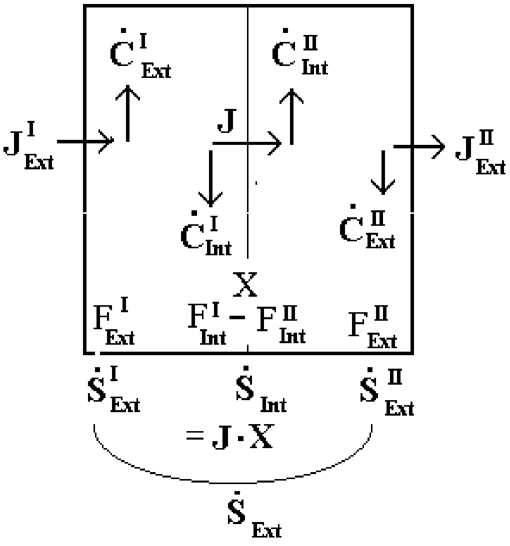


Fig. 7.

c. Local open system ('continuous phase')

$$\lambda \cdot \nabla(F \cdot \nabla j) = \lambda \cdot \nabla F \cdot \nabla j + \lambda \cdot F \nabla^2 j = \operatorname{div} J_S = -P_S + \dot{S} \qquad (139)$$

Here, the distinction 'internal–external' looses his sense. The situation will be illustrated by a simple example. Let a spatial distribution of the potential F (e.g., temperature) be exp $(-x^2)$. Let the conductivity and the capacity (e.g. the heat conductivity and the heat capacity) be unity.

Table 4.

			II.	III.	IV
		$x < \frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}} < x < 0$	$0 < x < \frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}} < x$
F	e^{-x^2}	> 0	> 0	> 0	> 0
J	$-2xe^{-x^2}$	> 0	> 0	< 0	< 0
$\mathrm{d}C/\mathrm{d}t$	$(4x^2 - 2) \cdot e^{-x^2}$	> 0	< 0	< 0	> 0
$P_S = J \cdot X$	$4x^2 \cdot e^{-2x^2}$	> 0	> 0	> 0	< 0
$\mathrm{d}S/\mathrm{d}t = -F \cdot \mathrm{d}C/\mathrm{d}t$	$-(4x^2 - 2) \cdot e^{-2x^2}$	< 0	> 0	> 0	< 0
$\nabla(F \cdot J)$	$(8x^2 - 2) \cdot e^{-2x^2}$	> 0	< 0	< 0	> 0

3.4. Evolution under Constraints

Extremum Principles

Two main types of constraints can be distinguished:

a. Constraints leading to equilibrium.
b. Constraints leading to non-equilibrium steady states.

a. Equilibrium Constraints

Under equilibrium constraints all potentials tend to equilibrate. The characteristic process of the evolution is the reduction of the gradients ∇F_i and of ∇j_i (ZL and DB),

$$(\dot{\nabla} F_i^2) < 0 \qquad \text{and} \qquad (\dot{\nabla} j_i^2) < 0, \qquad (140a)$$

$$\nabla F_i(\mathrm{Eq}) = 0 \qquad \text{and} \qquad \nabla j_i(\mathrm{Eq}) = 0. \qquad (140b)$$

Evolution of Entropy in an Isolated System

$$J_i \cdot \mathrm{d}\Omega = 0 \qquad (\text{all } i) \qquad (141)$$

where $\mathrm{d}\Omega$ is the normal vector of a surface element.

The entropy increases and has its maximal value at equilibrium.

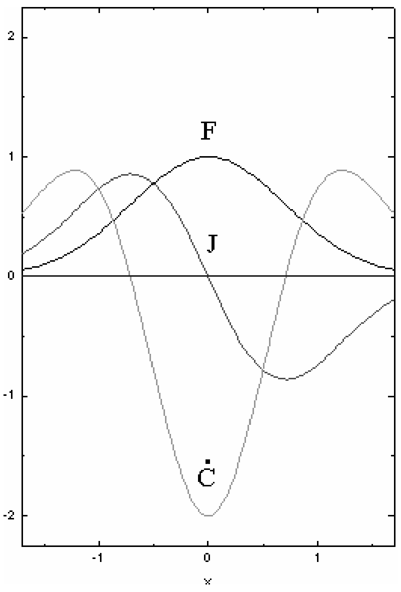


Fig. 8. Distribution of F, J, $\mathrm{d}C/\mathrm{d}t$

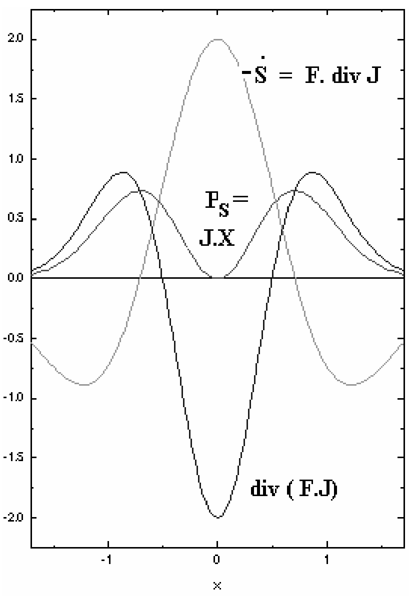


Fig. 9. Distribution of J_S, P_S and $\mathrm{d}S/\mathrm{d}t$

Other Equilibrium Constraints

In more general cases one or more potentials are held at constant value along the internal part of the system, leaving open the boundary for these fluxes. For the remaining fluxes the boundary is kept closed. (Constraint I.)

$$\nabla F_i = 0 \qquad J_i \cdot X_i = 0 \qquad (i = 1, \ldots, k) \tag{142a}$$

$$J_i \cdot \mathrm{d}\Omega = 0 \qquad \int \dot{C}_i \cdot \mathrm{d}V = 0 \qquad (i = k + 1, \ldots, n) \tag{142b}$$

From these inequalities several extremum principles follow.
Extremum of various Legendre transformed ‘potentials’ of entropy, such as:

Enthalpy (H):	isobaric system, closed for energy and mass (→ minimum),
Free energy (A):	isothermal, isosteric system (→ minimum),
Gibbs free energy (G):	isothermal isobaric system (→ minimum).

b. Steady Constraints

Consider a macroscopic system of volume V and boundary surface characterised by the normal vector Ω. Let be an initial distribution of properties C_i, j_i and F_i and their

Table 5.

The general kinetic law j_i and F_k has the form

$$-\mathrm{d}\ln j_i = \sum Q_{ik}\mathrm{d}F_k$$

$$\mathrm{d}j_i = \sum_k \Lambda_{ik}\mathrm{d}F_k$$

because the charges Q_{iz} are positive.

Matrix Λ is negative definite

(monotonity, stability)

$$\delta^2 Z = \sum_i \mathrm{d}_i \cdot \mathrm{d}F_i \le 0$$

$$\sum \Delta j_i \cdot \Delta F_i \le 0 \qquad \sum \nabla j_i \cdot \nabla F_i \le 0 \qquad \sum \dot{j}_i \dot{F}_i \le 0$$

$$\dot{P}_S = \sum J_i X_i \ge 0$$

Positivity of the ‘entropy Production’ is of unlimited validity.

$$\dot{H}_{\mathrm{int}} \ge 0 \qquad \dot{S} - \sum \nabla(F_i \cdot J_i) \ge 0 \qquad \dot{G}_{\mathrm{int}} \le 0$$

Isobaric, adiabatic — Isolated — Isobaric, isothermal

$(\dot{S}_{\mathrm{int}} \ge 0)$

The law of increase of entropy is only of limited validity

derivatives and binary products. Let some properties (e.g., the F_i’s) on the boundary be fixed and/or constrained (e.g., some external fluxes). The internal distribution of the properties of the system does then change in time. This evolution process is governed by the static and kinetic equations on one side and by the constraints of external origin on the other side. If no chemical transformations occur then the system tends to a stationary final state determined by the steady constraints

[29]–[33].

Integrals

The stationary constraint requires the overall conservation of the i'th quantity:

$$\oint J_i \cdot \mathrm{d}\Omega = 0 \qquad \text{or} \qquad \oint \Psi_i \cdot J_i \cdot \mathrm{d}\Omega = 0 \qquad \text{(Constr. II.)} \tag{143}$$

where: Ψ_i is a nonzero scalar quantity, and
Ω is the normal vector of the surface.

In the sense of the Gauss-theorem,

$$\oint (\Psi_i \cdot J_i) \cdot \mathrm{d}\Omega = -\int \nabla(\Psi_i \cdot J_i) \cdot \mathrm{d}V = 0. \tag{144}$$

The integral $\oint$ is taken over the closed surface and the volume integral over the volume of the system. The latter expresses the overall amount of the scalar divergence of the vector $(\Psi_i \cdot J_i)$. A next task is to find this scalar property, its components, determine the direction of their change in time and the (extreme) values at the steady state.

This property is not unique, depends on the factor Ψ_i. Some possible $(\Psi_i J_i)$ vectors are:

$$F_i \cdot J_i, \qquad \dot{F}_i \cdot J_i, \qquad C_i \cdot J_i, \qquad \dot{C}_i \cdot J_i.$$

The scalar spatial differentials are

$$\nabla(F_i \cdot J_i) = \nabla F_i \cdot J_i + F_i \cdot \nabla J_i = X_i \cdot J_i - F_i \cdot \dot{C}_i, \tag{145a}$$

$$\nabla(\dot{F}_i \cdot J_i) = \nabla \dot{F}_i \cdot J_i + \dot{F}_i \cdot \nabla J_i = \dot{X}_i \cdot J_i + \dot{F}_i \cdot \dot{C}_i, \tag{145b}$$

$$\nabla(C_i \cdot J_i) = \nabla C_i \cdot J_i + C_i \cdot \nabla J_i = -\frac{1}{D} J_i^2 - \frac{1}{2} \dot{C}_i^2, \tag{145c}$$

$$\nabla(\dot{C}_i \cdot J_i) = \nabla \dot{C}_i \cdot J_i + \dot{C}_i \cdot \nabla J_i = \nabla \dot{C}_i \cdot J_i - (\dot{C}_i)^2 \tag{145d}$$

Principle of the Minimum Entropy Production at Steady State

The sums of the products on the right side play different roles in process thermodynamics. Among them are, for example the entropy production, its X-type change in time, the entropy change, the entropy second differential and others.

The volume integrals of the product vectors on the left side (equal to the surface integrals) vanish at the stationary constraints and the appropriate volume integrals of the two products on the right side get equal.

$$\int \sum_i (X_i \cdot J_i) \cdot \mathrm{d}V = \int \sum_i (F_i \cdot \dot{C}_i) \cdot \mathrm{d}V \ \geq 0 \quad (\to \text{minimum}) \tag{146a}$$

$$\int \sum_i (\dot{X}_i \cdot J_i) \cdot \mathrm{d}V = \int \sum_i (\dot{F}_i \cdot \dot{C}_i) \cdot \mathrm{d}V \ \leq 0 \quad (\to \text{maximum}) \tag{146b}$$

$$\int \sum_i \left(\frac{1}{D} J_i^2 \right) \cdot \mathrm{d}V = - \int \sum_i \frac{1}{2} (\dot{C}_i^2) \cdot \mathrm{d}V \geq 0 \quad (\to \text{minimum}) \tag{146c}$$

$$\int \sum_i (\nabla \dot{C}_i t \cdot J_i) \mathrm{d}V = \int \sum_i (\dot{C}_i)^2 \mathrm{d}V \qquad \geq 0 \quad (\to \text{minimum}) \tag{146d}$$

In all definite quantities time rate occurs, the definiteness means not only 'force' arrow but 'time arrow' as well. For example, positivity of the Entropy Production does not mean anything about the sign of the time rate of change. Exactly, (146a) is the proof of the Principle of the Entropy Production Minimum. If the relation of J and X is linear,

$$J = L \cdot X, \qquad \mathrm{d}P = \mathrm{d}_J P + \mathrm{d}_X P, \qquad \mathrm{d}_J P = \mathrm{d}_X P. \tag{147}$$

Two remarks are to be mentioned.

In reality, the force is linear in $\Delta \ln j$ and not in Δj $(= -J)$. Consequently, force X is function of j and not alone of J (the relation is 'quasilinear'). A more serious problem comes for when, far from equilibrium (at phase transitions, chemical reactions) the force X is a finite difference of two exponentials. In such cases X is not a unique function of J at all. The non-exact differentials of P_S cannot be integrated, the property 'D' (called 'dynamic potential' by Prigogine) does not exist and the integral-principles cannot be applied.

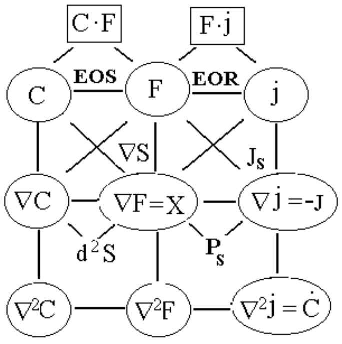


Fig. 10. Participants of thermodynamic relationships

Summary of results of Part 3.

1. The Second Law

"Natural" and "unnatural" processes and the Second Law

2. The Force Arrow

Monotonity of EOS and EOR state relations

The principle of Stability.

Definite state matrices.

Exact and non-exact differentials.

Second differentials.

(The Entropy Production).

3.The Time Arrow

Kinetic origins:

The Principle of Dissipation and the Mass-Action Law.

The Force Arrow and the Time Arrow.

The production of the entropy and the Entropy Production.

Examples:

Closed system. Open global system. Open local system.

4. Evolution under constraints

Extremum Principles.

Equilibrium constraints.

Entropy, enthalpy, free energy.

Steady constraints.

Integrals

"Theorem of the Minimum Entropy Production".

References

[1] GIBBS, J. W., *The Scientific Papers of J. W. Gibbs*, Dover Publ. New York, 1961.
[2] TISZA, L., *Generalized Thermodynamics*, MIT. Press, Cambridge, Mass., London, (1966), pp. 53–101.
[3] CALLEN, H. B., *Thermodynamics*, 1960, *Thermodynamics and an Introduction to Thermostatics*, Wiley, 1985.
[4] ATKINS, P. W., *Physical Chemistry*, IV. Ed., Oxford Univ. Press, 1990.
[5] OLÁH, K., *Periodica Polytechnica, Ser.Chem. Eng.*, **42**, (1997), pp. 21–32.
[6] MAXWELL, J. C., *Phil. Trans. Roy. Soc. London*, **157** (1867).
[7] OLÁH, K., Thermokinetics (An Introduction)., *Periodica Polytechnica*, **31** (1987), pp. 19–27.
[8] OLÁH, K., Thermostatics, Thermodynamics and Thermokinetics, *Acta Chim. Hung.*, **125** (1988), pp. 117–130.
[9] FOWLER, R. H., Statistical Equilibrium with Special Reference to the Mechanism of Ionisation by Electronic Impacts, *Phil. Mag.*, **47** (1924), p. 257.
[10] DIRAC, P. A. M., The Conditions for Statistical Equilibrium between Atoms, Electrons and Radiation, *Proc. Roy. Soc.*, **106A** (1924), pp. 581–596.
[11] THOMSEN, J. S., Logical Relations among the Principles of Statistical Mechanics and Thermodynamics, *Phys. Rev.*, **91**, (1953), pp. 1263–1266.
[12] KLEIN, M. J., Principle of Detailed Balance, *Phys. Rev.*, **97** (1955), p. 1446.
[13] DENBIGH, K. G., *The Thermodynamics of the Steady State*, Methuen, London, 1951.
[14] GULDBERG, C. – WAAGE, P., Études sur les affinités chimiques, Christiania, 1867.
[15] EINSTEIN, A. – EHRENFEST, P., *Z. Phys.*, **19**, (1923), p. 301.
[16] OLÁH, K. – BÓDISS, J., Generalized Form of the Kinetic Mass-Action Law, *Chem. Ing. Techn.*, **63** (1991), pp. 1019–1021.
[17] OLÁH, K. – BÓDISS, J., Kinetics of Atom-Photon Interactions. *Int. J. of Quantum Chemistry*, **53**, (1995) pp. 265–273.
[18] TOLMAN, R. T., *Phys. Rev.*, **23** (1924), p. 699.; *The Principles of Statistical Mechanics*, Oxford Univ. Press., London, (1938), sec. 122.
[19] BOLTZMANN, L., *Wien. Sitz.*, **66** (1872), p. 275.
[20] ANGELOPOULOS, A. et al.: *Phys. Lett. B.*, (1998) p. 444.
[21] OLÁH, K. – BÓDISS, J. – FARKAS, H., Thermodynamic Charges, *Acta Chim. Hung.*, **127** (1990), pp. 783–794.
[22] OLÁH, K., The Effective Activation Energy. A Thermokinetic Approach, *Acta Chim. Hung.*, **127** (1990), pp. 135–147.
[23] OLÁH, K., Time Reversal Symmetry in Thermodynamics, *ACH/Models in Chemistry*, **137** (2000), pp. 845–866.
[24] OLÁH, K. – FARKAS, H. – BÓDISS, J., The Entropy Dissipation Function, *Periodica Polytechnica*, **33** (1989), pp. 125–139.
[25] THOMSON, W., (Lord Kelvin), *Proc. Roy. Soc. Edinburgh*, 1854., p. 123. Coll. Papers I. pp. 237–241.
[26] ONSAGER, L., Reciprocal Relations in Irreversible Processes I-II., *Phys. Rev.*, **37** pp. 405–426., and **38** (1931), pp. 2265–2279.
[27] MEIXNER, J., Macroscopic and Microscopic Reversibility, *Reports on Math. Phys.*, **7** (1973), pp. 37–57.
[28] GLANSDORFF, P. – PRIGOGINE, I., Sur les propriétés différentielles de la production d'entropie, *Physica*, **XX** (1964), pp. 773–780.
[29] GLANSDORFF, P. – PRIGOGINE, I., *Thermodynamic Theory of Structure, Stability and Fluctuations*, Wiley-Interscience, New York, 1971.
[30] GLANSDORFF, P. – NICOLIS, G. – PRIGOGINE, I., The Thermodyn. Stability Theory of Non-Equil. States, *Proc. Nat. Acad. Sci. USA*, **71** (1974), pp. 197–199.
[31] GYARMATI, I., *Non-Equilibrium Thermodinamics, Field Theory and Variational Principles*, Springer, 1970.
[32] GYARMATI, I. – OLÁH, K., *Acta Chim. Hung.*, **35** (1963), pp. 95–105.
[33] OLÁH, K., *The Entropy Production. New Aspects*, in: Second Law Analysis of Energy Systems. Ed. E.Sciubba an M.J.Moran, Roma, 1995, pp. 165–179.
[34] FARKAS, H. – NOSZTICZIUS, Z., *Ann. d. Physik*, **27** (1971), pp. 341–348.
[35] KISS, E., *Periodica Polyt.*, **41** (1997), pp. 205–211.