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THERMOKINETICS OF THE EQUILIBRIUM STATE

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Abstract

This paper consists of two parts. In the first part the fundamental properties, balances, state spaces, relationships are recapitulated in a revised symmetrical and demonstrative form. The origins of the non-ideality are explained. It is known that a material system in thermodynamic equilibrium may be regarded as a "living" body nest of internal motions, processes, transformations (similar to the circulation of blood in the body of a living creature). In the second part the new theory '*Thermokinetics*' is applied to the dynamics of equilibrium systems. The basic processes are the "absolute rates" of exponential (and not linear) force law form. It is demonstrated that all types of physicochemical process rate relations can be derived from a central general rate equation. The three fundamental state spaces, the two main cross symmetries (one of them introduced by the author) and the general time reverse symmetry relations are discussed. It is shown that the general property of nature, the irreversibility is found to be a basic property of equilibrium systems.

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

Introduction

Thermodynamic system is a macroscopic multitude of microscopic elements (atoms, molecules, electrons, photons, phonons, etc.). Most of the systems we meet are in equilibrium or near to it, possessing pressure, temperature and chemical potentials.

A number of aspects are known for interpreting and describing thermodynamic systems and laws. There are a number of viewpoints, applications, aims. Contrary to the classical mechanics (e.g., motion of a single rigid body), the coordinates are fixed to a given point of place: 'local' vs. 'substantial' representation. Our discussion will be 'material-centered' (objectivistic) and not 'man-centered' (the viewpoint of observers, engineers, appliers). In this sense, we will mainly deal with 'processes' instead of 'operations'. The behaviour of the material in a vessel place depends mostly on its local environment and not on the distance from the wall of the container. 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 simple and 'nature-centered'. We strive to get rid of historical aspects, the 'Laws of Thermodynamics' (Zeroth, First, Second, Third Law) will not play dominant role in the framework of the theory. We will prefer entropic vs. energetic representation, because experiences proved that, it results in more simple formalisms (use of $1/T$ vs. T at describing temperature-dependences). In the last section we will strive for minimalizing the number of postulates.

1. Thermostatics

1.1. Thermodynamic System. The State Space. Invariant Extensive Quantities

It was Willard Gibbs who laid down the foundation of a systematic theory of macroscopic equilibrium systems [1]. The 'global' thermodynamic system is a finite region in space specified by a set of variables $E_1, E_2, \ldots E_n$. The E_i's form the set of the independent extensive, additive, conserved quantities ('invariants'). The most important ones are:

the internal energy (U),
the volume (V) and
the molarities of the independent chemical components (N_k) [2].

'Extensivity' means that the i'th property E_i of a system is proportional to the size of the system.

'Additivity' means that if the quantity E_i of a subsystem (I) is $E_i^{(I)}$ and that of the other subsystem (II) is $E_i^{(II)}$ then for the whole system

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

'Conservativity' means that if a quantity E_i passes from (I) into (II), then

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

independently from other properties (temperature, pressure, density, etc.) of the two subsytems, that may differ or not. (Conservative quantities are: U, V and excluding chemical transformation, N_k as well, non-conservative quantities are: temperature, entropy, enthalpy and others).

Gibbs' space: The application of geometrical methods to thermodynamics is based on the thermodynamic phase space called 'Gibbs space' of the E_i's, the basic 'coordinates' of this space [2]–[4]

$$(U, V, N_k).$$

Some other invariant extensive quantities are: the *surface* (in many cases the surface phases take part in the overall properties of a phase in a negligible degree), the *momentum* (if the mass center of the body is defined as to be in rest, the overall momentum is zero) and the *electric charge* (it plays significant role only if the 'electroneutrality' is violated).

Carried quantities: Some of the E_i's (e.g., the energy) are bound to material particles (molar or partial molar quantities, or 'charges' in a broad sense) [5].

Dimensionless version. Natural units. In many applications E_i's are placed on the exponent. In this case they must be divided by a 'natural unit'. The natural unit of the energy may be the quantity RT, where R is the gas constant ($R = 8.314$ J/Kmol) and T is the absolute temperature. RT is defined as

$$RT \equiv \lim_{P \to 0} (P \cdot V), \tag{3}$$

where P is the pressure and V is the mole volume of a gas. The natural unit of the mole numbers N_k may be the overall number of the chemical particles. The appropriate dimensionless quantity is the mole fraction (x_k)

$$x_k \equiv N_k / \sum_k N_k. \tag{4}$$

The unit of the volume may be an appropriate n-dimension 'characteristic volume' V^*, e.g., the average cell volume of the configuration phase space

$$V^* = \left(\frac{h_P}{p} \right)^n, \tag{5}$$

where h_P is the Planck constant and p is the average ('thermal') momentum.

Singularity problem. The number of variables of the state space defined above may be greater than the number of dimensions of the space. In other words, the variables are not 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. To avoid this problem it is advisable to use a 'local' system.

Local system: 'Local system' is a small area of given volume without any physical walls (open system). The space of states is then spanned by the densities (in other word, the *concentrations*), defined as

$$C_i \equiv \lim_{V \to 0} (E_i / V). \tag{6}$$

By definition, the density of the volume is unity and $\mathrm{d}V \equiv 0$. Consequently, the number of coordinates is less by one than that of the global system. This way, C_i's may form an independent set.

1.2. Entropy (S)

Entropy plays in Gibbs' thermostatics a central role. Entropy is an extensive, additive but *non-conservative* quantity. This property follows from the fact that entropy is essentially a sum of *products:* products of invariant extensive quantities (E_i) and other, 'intensive' factors (the potentials, F_i). It can be proved that if all E_i's are conservative, S cannot be conservative. Because of the 'non-conservativity' of S, there is no 'entropy flux' (the quantity called 'entropy flux' is a special product sum discussed later). There are other non-conservative thermodynamic quantities as well, such as enthalpy (H), Gibbs- and Helmholtz-free energy (G and A), etc. Fluxes in a non-equilibrium system are accompanied with 'production' of entropy (increasing in value without any outer supply). The characteristic unit of S is the gas constant (R). Entropy is closely related to the distribution of the elements of the system. To any (eventually irregular) distribution an exact entropy can be defined:

$$\frac{S}{R} = \sum_i \ldots \sum_k x_{i\ldots k} \ln x_{i\ldots k}, \tag{7}$$

where the $x_{i,\ldots,k}$'s are the fractions (not only probabilities) of the elements of the system in question, similar (indistinguishable) in one and different (distinguishable) in the other respect. No requirements prescribe the type of distinctions. The entropy is, consequently, optional to some extent [6]. The entropy of an energy distribution will be energy-dependent ('thermal'entropy). A distribution, (e.g., the isotopic composition) is to be taken into account only if it undergoes a change. If not, the appropriate entropy term is superfluous. This property of entropy results in the apparent contradictory statement that *entropy always exists.*

1.3. *First Derivatives of the Entropy. Potentials* (F_i)

In an equilibrium system the entropy is a homogeneous function of first order of the extensive state parameters:

$$\mathrm{d}S = \sum_i \left(\frac{\partial S}{\partial E_i}\right) \cdot \mathrm{d}E_i = \sum_i F_i \cdot \mathrm{d}E_i \quad (\mathrm{J/Kmol}). \tag{8}$$

The partial derivatives (F_i) are called the *'potentials'*:

$$F_i = \left(\frac{\partial S}{\partial E_i}\right). \tag{9}$$

Any density is accompanied by an appropriate potential.
The most important potentials are:

E_i	C_i	F_i
U	C_U	$1/T$
N_k	C_k	$-\mu_k/T$
V	1	P/T

where T is the absolute temperature (K),
μ_k is the chemical potential of the k'th component (J/mol),
P is the pressure (Pa).

Remind that use of the entropy- (vs. energy-) representation is justified by experiences.

To make plots using $1/T$ and $-\mu/T$ (against T and μ) is more advisable.

The potentials play important roles in thermodynamics:

a. Tendency towards equilibration (*transitivity*, 'Zeroth Law' in a general sense): If A is in equilibrium with B and B is in equilibrium with C then $F_A = F_B$ and $F_B = F_C$ and, consequently, $F_C = F_A$, i.e. A is in equilibrium with C.
b. Driving forces of physicochemical processes.

In such cases the *independency* is important. Constraints (e.g., ions carry electric charge, stoichiometric numbers connect changes of the constituents), as the set of potentials is to be transformed into an independent set (for example, the chemical potential is to be replaced by the 'electro-chemical potential', $\mu_e = \mu + z \cdot F \cdot \varphi$). All transformations must be carried out keeping the entropy invariant.

1.4. Energy and Entropy Balances. Gibbs Space

1.4.1. Global Balance

For a *global* system the energy balance writes

$$\overbrace{\underbrace{U - T}_{A} \cdot \underbrace{S + P \cdot V}_{-W}}^{H} - \overbrace{\sum_k \mu_k \cdot N_k}^{G} = 0. \tag{10}$$

Some combinations are defined and used :

$$\text{The Gibbs' free energy :} \quad G \equiv \sum_k \mu_k \cdot N_k = H - T \cdot S, \tag{11}$$

$$\text{The enthalpy :} \quad H \equiv U + P \cdot V = G + T \cdot S, \tag{12}$$

$$\text{The Helmholtz' free energy :} \quad A \equiv U - T \cdot S = G - P \cdot V, \tag{13}$$

$$\text{The Kramers potential :} \quad W \equiv T \cdot S - P \cdot V = U - G. \tag{14}$$

U, V, N_k are extensive, additive and *conservative* quantities.

S, H, A, G, W are all extensive and additive but *not conservative* quantities.

The characteristic variables are

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

Another ‘governing’ property of the Gibbs space is the entropy. The entropy balance:

$$\overbrace{\underbrace{S - V\cdot(P}_{W/T}\,/\,\underbrace{T) - U\cdot(1/T)}_{-H/T}}^{-A/T} - \underbrace{\sum_k N_k\cdot(-\mu_k/T)}_{-G/T} = 0. \tag{15}$$

1.4.2. The Balances of the Differentials. The Gibbs Equations

The energy balance:

$$\text{GIBBS}\qquad \mathrm{d}U = T\cdot\mathrm{d}S - P\cdot\mathrm{d}V + \sum_k \mu_k\cdot dN_k, \tag{16}$$

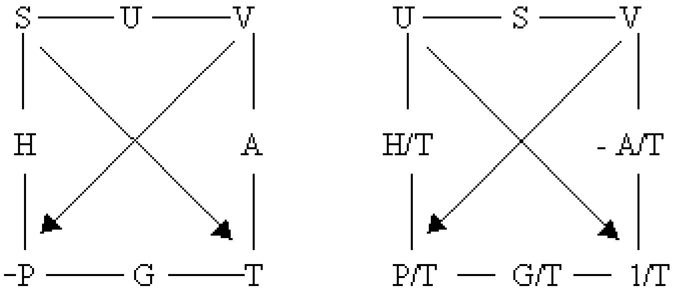
$$\text{GIBBS–DUHEM}\qquad 0 = S\cdot\mathrm{d}T - V\cdot\mathrm{d}P + \sum_k N_k\cdot\mathrm{d}\mu_k. \tag{17}$$

The entropy balance

$$\text{GIBBS}\qquad \mathrm{d}S = (1/T)\cdot\mathrm{d}U + \sum_k(-\mu_k/T)\cdot\mathrm{d}N_k + (P/T)\cdot\mathrm{d}V, \tag{18}$$

$$\text{GIBBS–DUHEM}\qquad 0 = U\cdot\mathrm{d}(1/T) + \sum_k N_k\cdot\mathrm{d}(-\mu_k/T) + V\cdot\mathrm{d}(P/T). \tag{19}$$

The interrelations can be illustrated using the *Born squares* ($\mathrm{d}N_k = 0$). The arrows point at the derivatives (opposite direction: negative).



(a) Born square (energy) (b) Born square (entropy)

Fig. 1.

As stated above, the number of variables is here greater than necessary by one. It proved to be more convenient to choose a local representation.

1.4.3. *Local System, Densities*

Calculating with densities of the extensive quantities, the superfluous variable, the volume disappears. (Densities do not depend on the volume). Taking $\mathrm{d}V = 0$ and dividing by V the densities form an independent set. Denoting the 'Kramers density' by Ψ

$$\Psi \equiv W/(TV) = S/V - P/T, \tag{20}$$

$$\Psi = (1/T) \cdot C_U + \sum_k (-\mu_k/T) \cdot C_k = \sum_j^n F_j \cdot C_j \ , \tag{21}$$

$$\mathrm{d}(S/V) = (1/T) \cdot \mathrm{d}C_U + \sum_k (-\mu_k/T) \cdot \mathrm{d}C_k = \sum_j^n F_j \cdot \mathrm{d}C_j , \tag{22}$$

$$\mathrm{d}(-P/T) = C_U \cdot \mathrm{d}(1/T) + \sum_k C_k \mathrm{d}(-\mu_k/T) = \sum_j^n C_j \cdot \mathrm{d}F_j . \tag{23}$$

S/V is the 'entropy density', the principal quantity of the *density space*,

$-P/T$ is principal quantity of the *potential space*, the Legendre transform of the entropy density. In general form,

$$F_i = \left(\frac{\partial\,(S/V)}{\partial C_i} \right), \qquad C_i = \left(\frac{\partial\,(-P/T)}{\partial F_i} \right). \tag{24}$$

An example: let the i'th term be the energy parameter. Then

$$C_i = \mathrm{tg}\,\beta = U/V, \tag{25}$$

$$F_i = \mathrm{tg}\,\alpha = 1/T. \tag{26}$$

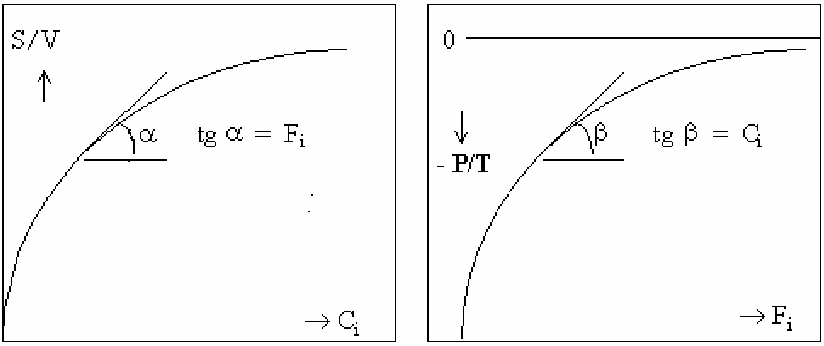
1.4.4. *The 'Second Differential' and the Second Law*

The set of the three fundamental product sums can be expanded with a fourth one, the 'second differential' of S/V defined as

$$\mathrm{d}^2(S/V) = \sum_j^n \mathrm{d}C_j \cdot \mathrm{d}F_j \le 0. \tag{27}$$

This product sum has very important function in thermodynamics. The negativity of $\mathrm{d}^2(S/V)$ is an important inequality of the *Second Law*.

The negativity may measure the *stability*: if $\mathrm{d}C_i$ means the deformation of the state and $\mathrm{d}F_i$ means the potential difference (the generated force) then the negativity means that the force is always a counter-force. The natural tendency is the diminishing of the absolute value of $\mathrm{d}^2\Psi$, i. e. the change in positive direction.



(a) Density space (b) Potential space

Fig. 2.

1.5. The Equations of State (EOS)

1.5.1. The State Matrix

At equilibrium the (independent) potentials are functions of the densities

$$\mathrm{d}F_i = \sum_k \Gamma_{ik} \cdot \mathrm{d}C_k \tag{28}$$

and inversely, the densities are functions of the potentials

$$\mathrm{d}C_i = \sum_k \Gamma_{ik}^{-1} \cdot \mathrm{d}F_k, \tag{29}$$

$$\Gamma_{ik} = \left(\frac{\partial F_i}{\partial C_k}\right) \quad \text{and} \quad \Gamma_{ik}^{-1} = \left(\frac{\partial C_i}{\partial F_k}\right). \tag{30}$$

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 of the state matrix are worth to mention.

Symmetry
Independency (rank)
Monotonity (definite)

1.5.2. Symmetry [7]

Γ_{ik}'s are the elements of the second derivative matrix of the entropy density and

Γ_{ik}^{-1}'s are the elements of the second derivative matrix of $-P/T$.

It follows from the elementary theorem of calculus that matrix $\mathbf{\Gamma}$ is always symmetrical

$$\Gamma_{ik} = \left(\frac{\partial F_i}{\partial C_k}\right) = \left(\frac{\partial^2 S/V}{\partial C_i \partial C_k}\right) = \left(\frac{\partial^2 S/V}{\partial C_k \partial C_i}\right) = \left(\frac{\partial F_k}{\partial C_i}\right) = \Gamma_{ki}, \tag{31}$$

$$\Gamma_{ik}^{-1} = \left(\frac{\partial C_i}{\partial F_k}\right) = \left(\frac{\partial^2 (-P/T)}{\partial F_i \partial F_k}\right) = \left(\frac{\partial^2 (-P/T)}{\partial F_k \partial F_i}\right) = \left(\frac{\partial C_k}{\partial F_i}\right) = \Gamma_{ki}^{-1}. \tag{32}$$

Maxwell's Reciprocity Relations (MRR)

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

1.5.3. Independency, the Rank

The ‘rank’ of a matrix is the number of its independent rows or columns. If the rank of an $n \times n$ matrix is n, then the set of variables is independent. If the rank is smaller than n, then the matrix is singular, there is dependence among rows or columns. In such case the determinant is zero and the reciprocal matrix cannot be evaluated.

1.5.4. Monotonity, Negativity and the Second Law

The potentials are dominant monotonic functions of the densities. In general, a matrix $\mathbf{A}$ is positive (or, negative) definite if for a system of linear equations

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

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

$$\mathbf{y} \cdot \mathbf{x} > 0 \quad (\text{or} < 0).$$

On the other side, definiteness of the matrix $\mathbf{A}$ means that $\mathbf{y}$ is monotonic function of $\mathbf{x}$. In our case, the entropy second derivative matrix is negative, in accordance with the negativity of the scalar $\mathrm{d}^2 S$ second differential.

$$\mathrm{d}^2(S/V) = \sum_i \mathrm{d}C_i \cdot \mathrm{d}F_i = \sum_i \sum_k \mathrm{d}C_i \cdot \Gamma_{ik} \cdot \mathrm{d}C_k \leq 0 \qquad \text{(II. Law)}. \tag{33}$$

The negativity involves a series of general inequalities. In a negative quadratic matrix all diagonal elements and all ratios D_n/D_{n-1} are negative, where D_n is the determinant of the $n \times n$ diagonal submatrix.

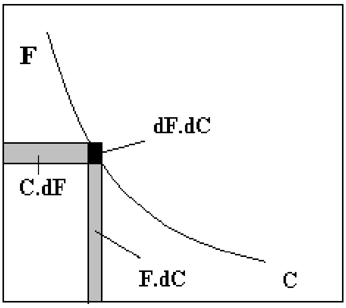


Fig. 3. Equation of state. Differentials

1.5.5. The Meaning of the Symbol ‘d’

Symbol ‘d’ may have various meanings, e.g., small changes, gradients, time rate of change, etc. Remaining at equilibrium, ‘d’ means a small displacement along an equilibrium hypersurface of the state space, governed by the EOS’s. The Gibbs- and the Gibbs–Duhem relations provide general interrelations between changes of densities and potentials.

1.6. Integrated Forms of the EOR’s. Ideal, Non-Ideal and Degenerated Systems

1.6.1. Ideal Systems

In some special cases the differential forms of the Gibbs and Gibbs–Duhem equations can be easily integrated leading to simple and evident form. The equations are called then ‘ideal’. Ideal systems are characterised by properties as follows.

a. Equipartition of energy. The energy (U) is proportional to the temperature (temperature-independent heat capacity):

$$\frac{U}{RT} = \frac{s}{2}, \tag{34}$$

where s is the number of degrees of freedom: for an n-atomic molecule $s = 3 \cdot n$, for an ideal atomic crystal $s = 6$.

b. No heat of mixing: In a mixture the partial energies (U_k) are composition-independent:

$$U_k = \frac{\partial U}{\partial x_k} \quad \text{and} \quad \frac{\partial U_k}{\partial x_k} = 0. \tag{35}$$

c. The ratio P/T is proportional to the overall number density (ideal gas)

$$\frac{P \cdot V}{RT} = 1 \quad \text{and} \quad \frac{P}{T} = R \cdot C. \tag{36}$$

d. The chemical potential is proportional to the logarithm of the mole ratio:

$$\frac{\mu_k}{RT} = \frac{\mu_k^0}{RT} + \ln x_k \quad \text{and} \quad \frac{\partial}{\partial x_k}\left(\frac{\mu_k^0}{RT}\right) = 0. \tag{37}$$

1.6.2. Non-Ideal Systems

Most state equations differ from the ideal forms because one or more ideality criteria are not valid.

The equipartition of the energy is a high-temperature limiting law. At low temperatures and/or for very restricted length of motion the equipartition is not valid. The basic parameter is the ratio of the average ('thermal') momentum $(2mkT)^{1/2}$ and the Planck constant. For usual temperature and masses this ratio, the 'thermal' length is in the order of magnitude

$$L^* \approx 10^{-11}\ \text{m}.$$

The free paths of the different kinds of motions are

Translation (one-atomic gas):	$L \approx 0.3$ m,	$L/L^* \approx 3.10^{10}$	Exact equipartition
Rotation of a molecule:	$L \approx 10^{-9}$ m,	$L/L^* \approx 100$	Near equipartition
Vibration of an atom:	$L \approx 10^{-11}$ m,	$L/L^* \approx 1 - 2$	Poor degree of excitation.

Because the distances of the allowed energy levels of the atomic vibrations are generally much larger than the average thermal energy, the degree of excitation is slight, its participation in the heat capacity is negligibly small.

Real gases. At increased densities a defect in the pressure is observed. The reason is the association: the number of particles is less than expected.

1.6.3. The Extended Hierarchy

A number of non-ideal phenomena are consequences of the fact that a given chemical component consists of *fractions* of different energy and/or configuration. The usual hierarchy of the thermodynamic system is simplified.

A more detailed hierarchy consists of five stages [8]:

- *Mixture*, composed of
  - *chemical components*, composed of
    - *fractions*, (different potential energies) composed of
      - *thermal* (different kinetic energies) fractions, owing more
        - *degenerate* (quantum) states, 'cells' of a phase space.

The fractions differ in potential energy due to the different *environments* (different chemical composition of the near-neighbour layers). Consequently, the fraction composition y_{kf} varies with the overall molecular composition x_k. In such case, though $\mathbf{U}_{kf}$'s are constants (ideality, bold), their average, U_k is composition-dependent (non-ideality, heat of mixing, 'excess' energy)

$$U = \sum_k x_k \cdot U_k, \tag{38}$$

$$U_k = \sum_f y_{kf} \cdot \mathbf{U}_{kf}. \tag{39}$$

Other deviations from the ideal values (excess chemical potentials, activity coefficients, excess entropy, etc.) can be interpreted in a similar way.

There are two important conclusions:

a. *A (chemically) one-component system may be mixture of fractions.*

b. *The fractions are in equilibrium with each other.*

1.7. Carriers, Carried Properties, Partial Molar Quantities

As explained above, the macroscopic thermodynamic system is an ensemble of elementary particles. Particles can be regarded elementary which cannot or need not be distinguished from each other. In an ideal system the chemical component molecules, in non-ideal mixture the fractions and so on, can be regarded as elementary particles,.

Let C_z^* be the density of the z'th kind of elementary component (z'th particles).

The z'th particle may represent ('carry') energy, momentum, electric charge, etc., and we will denote the amount of the i'th extensive entity carried by one mole of the z'th carrier particle (some kind of partial molar quantity) by P_{zi}. (E.g., the partial molar energy in a broad sense). The density of the i'th extensive invariant (e.g., the energy-density) is then

$$C_i = \sum_z P_{iz} \cdot C_z^*. \tag{40}$$

An obvious supposition is that P_{iz} is constant, independent of the number (or ratio) of the z'th particles. The Gibbs–Duhem relation can be written

$$\begin{aligned} \mathrm{d}(-P/T) &= -R \cdot \mathrm{d}C = -R \cdot \sum_z \mathrm{d}C_z^* = \\ &= -R \cdot \sum_z C_z^* \cdot \mathrm{d}\ln C_z^* = \sum_z C_z^* \cdot \mathrm{d}F_z^* = \sum_i C_i \cdot \mathrm{d}F_i. \end{aligned} \tag{41}$$

The potential of the z'th carrier can be defined as

$$\mathrm{d}F_z^* = -R \cdot \mathrm{d}\ln C_z^*. \tag{42}$$

Inserting P_{iz}

$$\begin{aligned} \sum_i C_i \cdot \mathrm{d}F_i &= \sum_i \left(\sum_z P_{iz} \cdot C_z^* \right) \cdot \mathrm{d}F_i \\ &= \sum_z C_z^* \cdot \left(\sum_i P_{iz}, \mathrm{d}F_i \right) = \sum_z C_z^* \cdot \mathrm{d}F_z^*, \end{aligned} \tag{43}$$

$$\mathrm{d}F_z^* = \sum_i P_{iz} \cdot \mathrm{d}F_i, \tag{44}$$

$$\left(\frac{\partial C_i}{\partial C_z^*} \right) = P_{iz} = \left(\frac{\partial F_z^*}{\partial F_i} \right). \tag{45}$$

E.g., the partial molar energy is on one hand the energy density (C_i) carried by the unit density of the carriers (C_z^*) and, on the other hand, the resultant force ($\mathrm{d}F_z^*$) acting on the z'th carrier is the sum of the macroscopic forces ($\mathrm{d}F_i$) multiplied by the appropriate P_{iz} quantities. (The temperature acts on the number of z'th carrier particles if it carries energy).

2. The Dynamic Equilibrium

Thermokinetics

Despite all appearances the equilibrium is not a dead state. A material body is a living organisation, nest of intensive internal processes. The materials are organisms

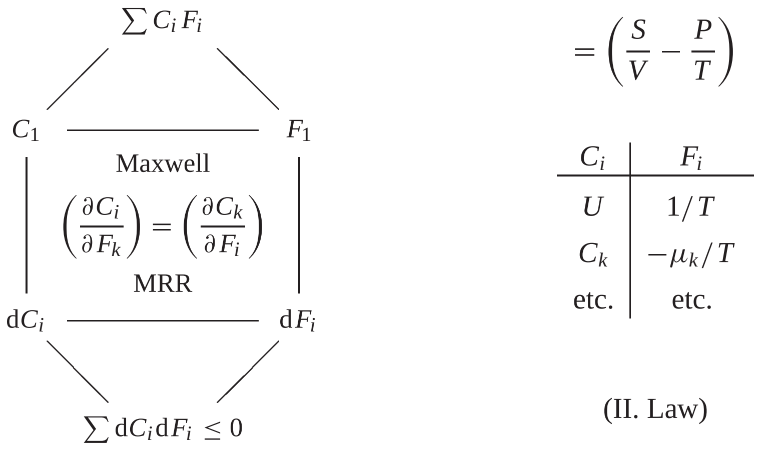


Fig. 4. Thermostatics. Summary of relations

of a great number of particles swarming in continuous motion, with velocities of more hundreds meters per second. They are migrating, rotating, vibrating, colliding, transforming with frequencies of billions per second. This dynamics drives the evolution towards the equilibrium state (the appropriate point attractor) and restores this state after any external perturbation. The dynamics provides temperature, pressure, chemical potential and entropy to the body. The characteristics of these rate processes, their rate equations and symmetries determine the observed macroscopic properties.

2.1. Processes Inside the Equilibrium Body

2.1.1. The Absolute (Unidirectional) Process Rates

In the kinetic theory ‘Thermokinetics’ the ‘absolute’ process rates play dominant roles [9, 10, 11]. The thermodynamic system differs from the mechanical one as the former consists of a great number of similar elements (particles). The word ‘thermo’ means that the system has temperature in a good approximation. The three fundamental groups of physicochemical processes are:

a. Transfers through an interface of two (equilibrated) phases:

   vaporisation/condensation through a liquid–vapour surface,
   solution/precipitation on a solid/liquid interface,
   electric charge transfer on a metal/electrolyte interface,
   heat transfer from a phase into another phase, etc.

   The transfer process rate ($j_i^{\rightarrow}$ or $j_i^{\leftarrow}$, moles/m^{2}s) is the product of the surface density (moles/m^2) and a frequency (1/s).

b. Fluxes inside a homogeneous phase:

diffusive or convective mass fluxes,
heat flow carried by molecules, electrons, phonons, photons, . . .
flux of momentum,
electric conduction carried by electrons or ions.

The process rate, e.g., flux of energy (J/m^{2}s) is the product of the energy density (J/m^3) and a velocity (m/s).

c. Scalar processes:

chemical transformations,
relaxation processes (restoring the equilibrium distribution).

The process rate is the product of a density and a frequency (moles/m^{3}s).

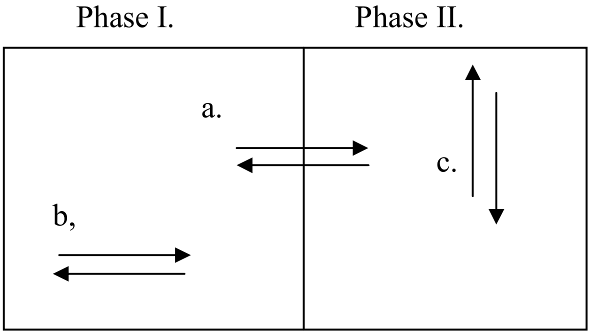


Fig. 5. Types of internal processes

The equal length of the opposite arrows symbolises the dynamic equilibrium state.

2.1.2. Reverse Process Rates. Law of Detailed Balance

All these processes have some kind of duality. Any elementary event may take place in an opposite direction. Such reverse process pairs are in time-reverse relation with each other. This kind of general feature of thermodynamic processes was put in words by FOWLER (1924) [12]: '*any one process of exchange acting in a particular direction must be invariable accompanied by an analogous reverse process*'.

Paul DIRAC wrote [13]:

> ‘*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 at the macroscopic level as well. At equilibrium all reverse macroscopic absolute process rates ($j^{\rightarrow}$ and $j^{\leftarrow}$) equilibrate

$$j_i^{\rightarrow}(\mathrm{eq}) = j_i^{\leftarrow}(\mathrm{eq}) \quad (\mathrm{DB}). \tag{46}$$

Examples: chemical reaction ‘from left to right’ and ‘from right to left’, evaporation and vapour condensation, in gases the fluxes of particles in directions $+x$ and $-x$ and the anodic and cathodic exchange current on electrode surfaces.

2.1.3. Carriers and Carried Properties. The Charges

Any process is carried by flow or transfer of elementary carriers (e.g., atoms, molecules, electrons, photons, phonons, other quasiparticles) [14]. The word ‘elementary’ means that the particles can be regarded structureless mass points or, their internal structure does not change during the process in question. The absolute flux (transfer, transformation) of the i’th (additive conservative) quantity is

$$j_i = \sum_i Q_{iz} j_z^*, \tag{47}$$

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.

Charges connect carriers and carried process rates

$$Q_{iz} = \left(\frac{\partial j_i}{\partial j_z^*}\right). \tag{48}$$

The four most important charges are:

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

$$Q_{\mathrm{el}} = z_k \cdot F, \tag{49}$$

where z_k is the value of charge of the k’th ion, and F is the Faraday charge.

b. The molar momentum (velocity):

$$Q_P = M_k \cdot u, \tag{50}$$

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

c. The stoichiometric coefficients ν_{ki} (affinity) [15]: the number of the k'th particle as participants in the i'th process.

d. The thermal charge is the most important one [16]:

$$Q_T = E^* + n \cdot RT. \tag{51}$$

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'. The thermal charge shows exact reverse symmetry:

$$E^{*\rightarrow} = E^{*\leftarrow} \quad \text{and} \quad n^{\rightarrow} = n^{\leftarrow}. \tag{52}$$

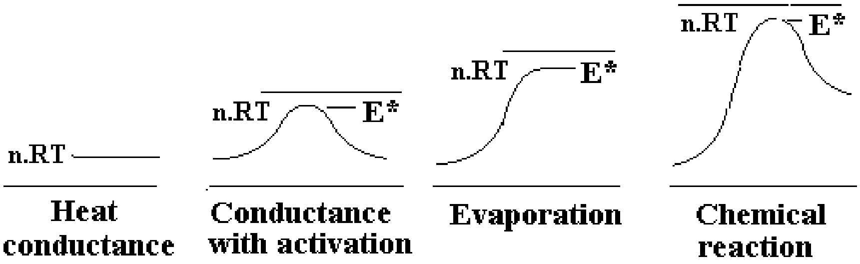


Fig. 6. Physical meanings of the thermal charge

2.1.4. *The Kinetic Mass Action Law (MA). The Rate Constant*

The absolute process rate is formulated as function of the densities of the participants

$$j_i(C_1 \ldots, C_n).$$

In the usual form

$$j = k \cdot \prod_k C_k^{\nu_k}. \tag{53}$$

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

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

This law called the '*Mass Action Law*' (MA) is declared by GULDBERG and WAAGE, in 1872. [17]. The law 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, all calculated with rate equations of MA type. It is to be noted that k is a function of temperature. The law seems clear and evident. Though, in numerous instances problems arose. One of them is the kinetic model of the light matter equilibrium by Albert EINSTEIN, [18] where MA leads to some contradictions. Another: chemical processes taking place in non-ideal mixtures. Here, 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 [19, 20]).

2.1.5. The Law of Microscopic Reversibility (MR)

The name 'Microscopic Reversibility' was given by R.T. TOLMAN [21]. TOLMAN's interest was elicited by EINSTEIN's paper dealing with the mass-radiation equilibrium [18]. In 1924 a paper was published by Tolman referring to that of Einstein. Tolman guessed that the equality of two rate constants supposed by Einstein 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*'. For many years the notions microscopic reversibility, detailed balance, steady state and equilibrium had been confusing. The law MR asserts that *the rate constants of the reverse process rates are equal*

$$k^{\rightarrow} = k^{\leftarrow}. \tag{54}$$

It is to be emphasized, however, that at 'macroscopic' processes this law is not valid any more. For example, to the rate constants of a chemical reaction

$$\begin{gathered} A \leftrightarrow B + C, \\ j^{\rightarrow} = k^{\rightarrow} \cdot C_A \quad \text{and} \quad j^{\leftarrow} = k^{\leftarrow} \cdot C_B \cdot C_C \end{gathered} \tag{55}$$

and

$$k^{\rightarrow} \neq k^{\leftarrow}. \tag{56}$$

The answer to this question is: *the law of MR is valid if the participants are 'ultimate', structureless particles*, or, their internal structure does not undergo any change during the given process.

They can be handled as simple mass points. (The participants may be of macroscopic size, e.g., ideal, elastic billiard balls). In our case, because the chemical reaction leaves the atoms (atomic nuclei) intact, the left and the right side contains really the same number of atoms (n). The overall number of the degrees of freedom ($3 \cdot n$) is the same at both sides. Any atomic particle (free or bound to other atoms in a molecule) of the same temperature has an average momentum $\mathbf{p}$ (for an ideal gas $\mathbf{p}$

= $(2\pi \text{m.kT})^{1/2}$) and a characteristic length ('thermal de Broglie wavelength', $h_P/\mathbf{p}$) or a characteristic volume V^*, the volume of an average cell of the phase space. The microscopic kinetics governs the evolution of the distribution of the particles in the accessible volume of the phase space, developing equilibrium occupation numbers (N_s^*) of the cells. The MA kinetics has in the sense of MR reverse symmetry:

$$j_{s\to z} = k_{s\to z} \cdot N_s = k_{z\to s} \cdot N_z = j_{z\to s} \tag{57}$$

and

$$k_{s\to z} = k_{z\to s}. \tag{58}$$

But, if the size of the phase space of the reactants (left side) differs from that of the products (right side) then the global average rate constants lose the reverse symmetry.

2.2. The Potentials. Kinetic Background

2.2.1. The Pressure as the Absolute Flux of the Momentum

The pressure is the flux density of the momentum carried by flux of molecules (gas) or phonons (condensed phases), as the 'carriers'. Other particles, e.g. photons exert in general negligible effects. Let it be the absolute flux of the particles in a given (x) direction, supposing that one half of the particles is moving in the positive x-direction

$$j_x^{\rightarrow} = 1/2 \cdot C \cdot |u_x| \;:\; j_x^{\leftarrow} = 1/2 \cdot C \cdot |u_x| \qquad (\text{mol/m}^2\text{s}), \tag{59}$$

where u_x is the average absolute velocity in a direction $+x$.

The particle flux carries the molar average momentum

$$p_x = M \cdot u_x \qquad (\text{kg} \cdot \text{m/mol} \cdot \text{s}). \tag{60}$$

Let the mass center of the local system be in rest, then all momentum fluxes and their opposite pairs must be compensated.

$$P = j_{p,x}^{\rightarrow} = 1/2 \cdot \rho \cdot u_x^2 = j_{p,x}^{\leftarrow} \qquad (\text{kg/m} \cdot \text{s}^2). \tag{61}$$

P is, in this sense, the average kinetic energy density.

2.2.2. The Temperature. Zeroth Law

The macroscopic definition of the absolute temperature is

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N_k}. \tag{62}$$

The system has temperature only if the energy is a unique function of the entropy.

Because the entropy represents the distribution of the elements (particles) of the system, the temperature measures the energy distribution:

$$\frac{1}{T} = -R \cdot \frac{\mathrm{d}\ln x_i}{\mathrm{d}\varepsilon_i}, \tag{63}$$

where x_i is the relative population of the energy ε_i.

All systems composed of a multitude of elements of different energies, the general kinetic feature results the tendency to establish a common temperature inside a given phase and equalising the temperature of any different phases in thermal contact.

The dynamics of the evolution of a stationary distribution is controlled by general laws and restrictions. Let our example be the energy transfer during collisions of particles (without any internal structure)

$$A_i + B_j \quad \leftrightarrow \quad A_k + B_l.$$

a. The Law of Mass Action: the energy-exchange process rate is proportional to the product of the numbers of the participants (the probabilities are multiplicative).

b. All elementary processes are reversible: each kind of encounter and its reverse occurs simultaneously.

$$\mathrm{d}C_i/\mathrm{d}t = -\sum_j \sum_k \sum_l (k_{ij,kl} \cdot C_i \cdot C_j - k_{kl,ij} \cdot C_k \cdot C_l). \tag{64}$$

c. The energies are additive (energy balance, EB).

$$\varepsilon_i - \varepsilon_k = \varepsilon_l - \varepsilon_j. \tag{65}$$

d. The rate constants of the reverse rate equations are all identical (Law of MR).

$$k_{ij,kl} = k_{kl,ij}. \tag{66}$$

e. At equilibrium all reverse rates equilibrate (DB).

$$C_i \cdot C_j = C_k \cdot C_l, \tag{67}$$

$$\ln C_i - \ln C_k = \ln C_l - \ln C_j \tag{68}$$

and

$$\frac{1}{T} = -R \cdot \frac{\ln C_i - \ln C_k}{\varepsilon_i - \varepsilon_k} = -R \cdot \frac{\ln C_l - \ln C_j}{\varepsilon_l - \varepsilon_j}. \tag{69}$$

The energy exchange processes result in that the points on the $E_i / \ln x_i$ plot are at last positioned along a straight line of a definite slope (common temperature) and intercept (chemical potential). If not, the system has neither temperature nor chemical potential.

Zeroth Law : Particles A and B may belong to the same phase (internal temperature relaxation) or particles of two energy levels of two different phases may be in thermal contact (transitivity of the temperature, the Zeroth Law)

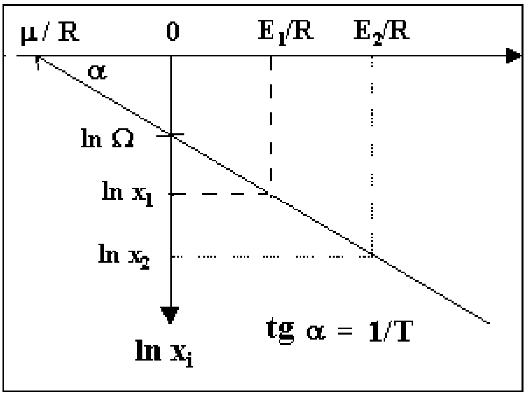


Fig. 7. Distribution, temperature, chemical potential

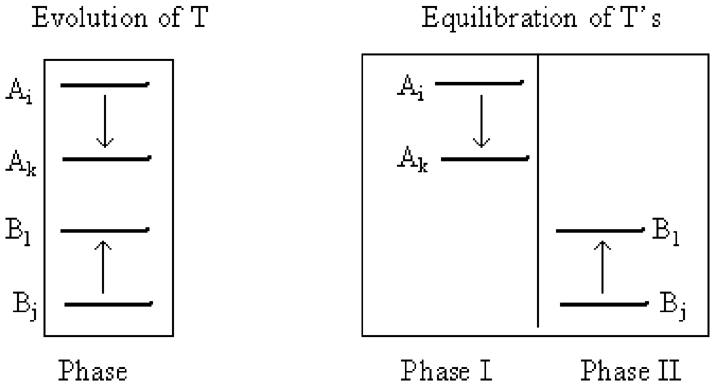


Fig. 8. Equalization of temperature

2.2.3. The Chemical Potential

As it was illustrated on the simple model, the relaxation process develops a chemical potential and an intercept with the energy axis. The chemical potential is always negative and temperature-dependent. The chemical potential of the A'th component varies with the relative number of the A'th particle

$$\frac{\mu_A}{RT} = \frac{\mu_A^0}{RT} + \ln x_A. \tag{70}$$

In kinetic equations it is more practical to use the exponential form:

$$\exp\left(\frac{\mu_A}{RT}\right) = \exp\left(\frac{\mu_A^0}{RT}\right) \cdot \frac{C_A}{C}. \tag{71}$$

The first term on the right side has a physical meaning worth to investigate. For the sake of simplicity regard a monoatomic ideal gas:

$$\exp\left(-\frac{\mu_A^0}{RT}\right) = \left(\frac{p \cdot L}{h_P}\right)^3 = \frac{V}{V^*}, \tag{72}$$

where $\mathbf{p}$ is the average momentum of the particles in the direction of L,
L is the length of the free displacement and V is the molar volume:

$$V = L^3, \tag{73}$$

h_P is the Planck constant,
h_P/p is the average ('thermal') de Broglie wavelength,

$$V^* = \left(\frac{h_P}{p}\right)^3 \tag{74}$$

is the volume of a phase cell (in the order of magnitude 10^{-33} m^3).

The exponent of the chemical potential is in our case the relative average number of particles A in a cell of the phase space accessible for A.

$$\exp\left(\frac{\mu_A}{RT}\right) = \frac{V^*}{V}\frac{C_A}{C} = \frac{C_A^*}{C}. \tag{75}$$

2.2.4. *The Charges Connect Carrier and Carried Potentials*

A carrier potential F_z^* can be defined as follows:

$$\begin{aligned}\sum_i j_i \cdot \mathrm{d}F_i &= \sum_i \left(\sum_z Q_{iz} \cdot j_z^*\right) \cdot \mathrm{d}F_i \\ &= \sum_z j_z^* \cdot \left(\sum_i Q_{iz} \cdot \mathrm{d}F_i\right) \\ &= \sum_z j_z^* \cdot \mathrm{d} \cdot F_z^*, \end{aligned} \tag{76}$$

$$\mathrm{d}F_z^* = \sum_i Q_{iz} \cdot \mathrm{d}F_i. \tag{77}$$

The double role of the charges can be formulated as

$$\left(\frac{\partial j_i}{\partial j_z^*}\right) = Q_{iz} = \left(\frac{\partial F_z^*}{\partial F_i}\right). \tag{78}$$

2.3. *The Dynamic Potential (Z)*

'Dynamic Potential' is the product sum defined as

$$Z \equiv \sum_i j_i \cdot F_i . \tag{79}$$

(Kinetic equivalent of the Kramers density, but with j_i instead of C_i).

The exact differential of Z is:

$$\mathrm{d}Z = \sum_i F_i \cdot \mathrm{d}j_i + \sum_i j_i \cdot \mathrm{d}F_i = \mathrm{d}Z_S + \mathrm{d}Z_P . \tag{80}$$

(Z_S is the equivalent of S/V and Z_P is that of P/T.) The first derivatives are:

$$F_i = \left(\frac{\partial Z_S}{\partial j_i}\right); \qquad j_i = \left(\frac{\partial Z_p}{\partial F_i}\right). \tag{81}$$

2.3.1. *The Dynamic Fundamental Balances*

For energy and mass transport, the dynamic fundamental balances are:

$$Z \equiv (1/T) \cdot j_U + \sum_k (-\mu_k/T) \cdot j_k , \tag{82}$$

$$\mathrm{d}Z_S = (1/T) \cdot \mathrm{d}j_U + \sum_k (-\mu_k/T) \cdot \mathrm{d}j_k , \tag{83}$$

$$\mathrm{d}Z_P = j_U \cdot \mathrm{d}(1/T) + \sum_k j_k \mathrm{d}(-\mu_k/T). \tag{84}$$

If $\mathrm{d}j_i$ means the finite difference J_i, then Z_S is the original form of the 'entropy flux'. In a more general form:

$$Z = \sum_i j_i \cdot F_i , \tag{85}$$

$$\mathrm{d}Z_S = \sum_i F_i \cdot \mathrm{d}j_i , \tag{86}$$

$$\mathrm{d}Z_P = \sum_i j_i \cdot \mathrm{d}F_i = \sum_z j_z^* \cdot \mathrm{d}F_z^* . \tag{87}$$

As can be seen, Z_P is a Legendre-transformed of Z_S. As Z_S is the principal dynamic quantity of the *kinetic (j) space*, Z_P is the same for the *potential (F) space*.

The mean products can be demonstrated on the $F - j$ plane (see *Fig.* 10).

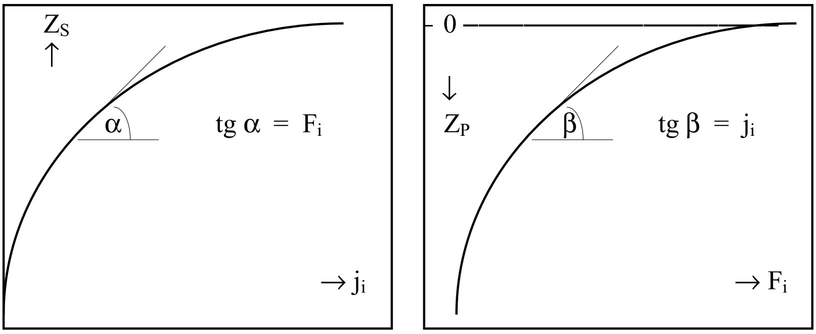


Fig. 9. Z_S in the dynamic space Z_P in the potential space

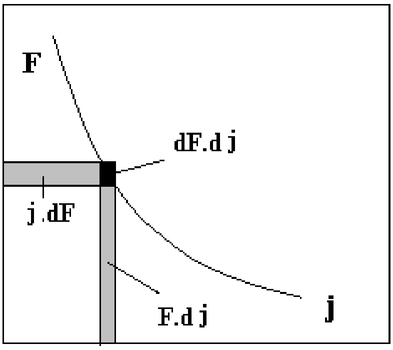


Fig. 10. The $j - F$ space

2.4. The Equations of Rates (EOR)

The absolute rates can be expressed in terms of several variables. Two main types of rate relations are distinguished.

2.4.1. The Conventional $j(P, T, C)$ Absolute Rate Equations

The experimental observations provide direct information about the pressure, temperature and composition (concentrations). This fact follows from the properties of the measuring instruments. Less convenient is to measure (and regulate) the ratio P/T and the chemical potentials. The most important physicochemical process rates are thus mostly described as functions of T, P and C_k. These rate equations, consequently, are of very different forms, a possible unified form is unrecognisable.

A series of such rate equations is:

1. Heat conduction: $j = j^0 \cdot T^n$
2. Heat radiation: $j = j^0 \cdot T^4$
3. Evaporation: $j = j^0 \cdot T^{1/2} \cdot \exp(-\Delta H_{\text{vap}}/RT)$
4. Condensation of vapor: $j = j^0 \cdot T^{1/2} \cdot P/RT$
5. Diffusion (gas): $j = j^0 \cdot T^n \cdot C$
6. Diffusion (liquid): $j = j^0 \cdot T^n \cdot \exp(-\Delta H_{\text{diff}}/RT)$
7. Chemical reaction $(A + B \rightarrow)$: $j = j^0 \cdot T^n \cdot \exp(-\Delta H_{\text{act}}/RT) \cdot C_A \cdot C_B$

Note: 3. and 4. are reverse of each other, showing quite different temperature-dependences!

2.4.2. The Potential-Action (PA) Rate Equations

PA type rate equations are called relationships where the absolute process rates are expressed in terms of the potentials (F_i)

$$j_i(F_1, \ldots, F_n), \tag{88}$$

where the variables F_i form the set of independent potentials:

reciprocal temperature $1/T$,
chemical potential $-\mu_k/T$,
electrochemical potential $-(\mu_k + z_k, F \cdot \varphi)/T$,
affinity (forward) $-(\sum_k \nu_k^{\rightarrow} \cdot \mu_k)/T$.

MA is represented in the configurational space, while PA in the potential-space. The use of PA has more advantages.

2.4.3. The PA Rate Equations Are Time Reverse Symmetrical

Two important general laws are valid for any equilibrium state:

a. *The (generalised) Zeroth Law*: at any equilibrium state all independent potentials equalise (transitivity)

$$F_i^{\text{eq}}(I) = F_i^{\text{eq}}(II) \qquad (ZL), \tag{89}$$

where I and II mean two parts of a thermodynamic system.

b. *The Law of Detailed Balance*: at any equilibrium state any process rate and its time reverse one equalise (‘in all details’):

$$j_{i,}^{\rightarrow} = j_i^{\leftarrow} \qquad (DB). \tag{90}$$

c. *The Law of macroscopic Reversal Symmetry.*
As a direct consequence of ZL and DB the time reverse rate equations of PA types are *identical*

$$j_i^{\rightarrow}(F) \equiv j_i^{\leftarrow}(F) \qquad (RS) \tag{91}$$

not only in the mathematical forms but for all constant parameters.

$$E^{*\rightarrow} = E^{*} = E^{*\leftarrow}, \tag{92}$$
$$n^{\rightarrow} = n = n^{\leftarrow}. \tag{93}$$

If it was not the case, neither DB, nor ZL would be satisfied for all possible equilibria. This statement reminds us to the MR, where the single constant parameter, the rate constant was only in very simple (microscopical) processes symmetrical ($k^{\rightarrow} = k^{\leftarrow}$). In other words: any process rate and its time reverse are in their physical properties quite identical. They are not two different processes but only a single one viewed from two directions. (In the sense of Newton’s law, the two forces, the one exerted by A on B and the reverse one exerted by B on A, are really only a single force, an *interaction* between A and B). As a striking example the evaporation–condensation process pair can be mentioned.

$$\begin{tikzcd}
\begin{array}{c} j^{\rightarrow}(T) = j^0 \cdot T^{1/2} \exp(-\Delta H_{\text{vap}}/RT) \\ \text{Evaporation} \end{array} \arrow[dr] & & \begin{array}{c} j^{\leftarrow}(T, P) = j^0 \cdot T^{1/2} \cdot P/RT \\ \text{Condensation} \end{array} \arrow[dl] \\
& \begin{array}{c} \text{Common } PA \text{ form:} \\ j^{\rightarrow}(1/T, -\mu/T) \equiv j^{\leftarrow}(1/T, -\mu/T) = \\ = j^0[T^{1/2} \cdot \exp(-E^*/RT)] \cdot \exp(\mu/RT) \end{array} &
\end{tikzcd}$$

2.4.4. Cross Effects. Cross Symmetry

The differentials of j are

$$\mathrm{d}j_i = \sum_k \Lambda_{ik} \cdot \mathrm{d}F_k, \tag{94}$$

where coefficients Λ_{ik} map the process rate space into the potential space. Cross effect is called the interdependence of the i’th flux and the k’th potential:

$$\Lambda_{ik} \neq 0 \qquad (i \neq k).$$

The origin of the cross effect is interpreted using the notion ‘charges’:

In such cases two or more processes may interfere with each other. Cross effects have been discussed by many authors. The earliest of them is W. Thomson about the thermoelectric phenomena. In general, the following can be stated: Any potential (or force field) assumes an appropriate charge. 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. The cross effect can be defined as follows: *Cross effect exists if one particle flux carries two or more different charges.*

Reciprocities. In such cases reciprocities were observed. It is plausible to suspect that the reciprocity may be a general property of processes. The cross symmetry ('Dynamical Reciprocity Relation', DRR) is the symmetry of the matrix of Λ_{ik}'s.

Cross symmetry is a consequence of several general facts. One of them is the *existence of the product sums* Z_P *and* Z_S.

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.

$$\Lambda_{ik} = \left(\frac{\partial j_i}{\partial F_k}\right) = \left(\frac{\partial^2 Z_p}{\partial F_i \partial F_k}\right) = \left(\frac{\partial^2 Z_p}{\partial F_k \partial F_i}\right) = \left(\frac{\partial j_k}{\partial F_i}\right) = \Lambda_{ki}, \tag{95}$$

$$\Lambda_{ik}^{-1} = \left(\frac{\partial F_i}{\partial j_k}\right) = \left(\frac{\partial^2 Z_s}{\partial j_i \partial j_k}\right) = \left(\frac{\partial^2 Z_s}{\partial j_k \partial j_i}\right) = \left(\frac{\partial F_k}{\partial j_i}\right) = \Lambda_{ki}^{-1}, \tag{96}$$

$$\Lambda_{ik} = \Lambda_{ki} \tag{97}$$

The Dynamic Reciprocity Relations (DRR)

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

2.4.5. The General Rate Law

It is possible to find a unified, general form for the rate equations. Analysis of all fundamental physicochemical processes leads to rate equations of universal form [22, 23]. This governing law is an *exponential* force law. This fact was to be expected: the process rates are in general proportional to the products of the numbers (probabilities) of the participants while the forces are additive

$$-R \cdot \mathrm{d} \ln j_z^* = \sum_k Q_{kz} \cdot \mathrm{d}F_k, \tag{98}$$

$$j_i = \sum_z Q_{iz} \cdot j_z^* \tag{99}$$

remind that

$$\begin{aligned} -\,R \cdot \mathrm{d} \ln j_z^* &= \mathrm{d}F_z^*, \\ \mathrm{d}Z_P = -\,R \cdot \sum_z \mathrm{d}j_z^* &= -R \cdot \sum_z j_z \cdot \mathrm{d} \ln j_z \\ &= \sum_k \left(\sum_z j_z^* \cdot Q_{kz} \right) \cdot \mathrm{d}F_k = \sum_k j_k \cdot \mathrm{d}F_k. \end{aligned} \tag{100}$$

The relation of j_i and F_k is, supposing that the Q's are constant

$$\mathrm{d}j_i = -1/R \cdot \sum_k \left(\sum_z Q_{iz} \cdot j_z^* \cdot Q_{zk} \right) \cdot \mathrm{d}F_k = \sum_k \Lambda_{ik} \cdot \mathrm{d}F_k. \tag{101}$$

Taking into account that Q may depend on some potentials (the thermal charge is temperature-dependent) the symmetry is valid :

$$\Lambda_{ik} = -1/R \cdot \sum_z j_z^* \cdot \left(Q_{iz} \cdot Q_{kz} + \frac{\partial^2 F_z^*}{\partial F_i \cdot \partial F_k} \right) = \Lambda_{ki}. \tag{102}$$

DRR is the symmetry of the matrix of the Λ_{ik}'s. An alternative proof for DRR has been given here. The sum in the brackets (Λ_{ik}) is invariant against interchanging i and k.

Example: mass and heat transfer.

The thermal potential:	$F_1 = 1/T$
The material potential:	$F_2 = -\mu/T$
The thermal charge:	$Q_1 = E^* + n \cdot RT$
The material charge:	$Q_2 = \nu (= 1 \text{ or } \nu_A, \nu_B)$

The integral form is:

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

$$\mu = \mu^0 + RT \cdot \ln C.$$

The integrated form of the absolute rate equations of heat/mass transfers is

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

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

$$\frac{\mu^0}{RT} = \frac{E}{RT} - \frac{S^0}{R} + \ln \frac{C}{\Sigma C}.$$

Let be

$$E^* - E = \Delta E^*$$

and let S^0, $\sum C$ be constant,

$$j = j^0 \cdot \exp(-\Delta E^*/RT) \cdot C.$$

(S^0 depends on the energy-distribution and on the extension of the phase space volume).

Inserting different charges the appropriate process rate relations are resulted (*Table 1*):

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	$j = j^0 \cdot T^{1/2} \cdot \exp(-\Delta H_{\text{vap}}/RT)$	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

2.5. *The Second Differential of the Dynamic Potential*

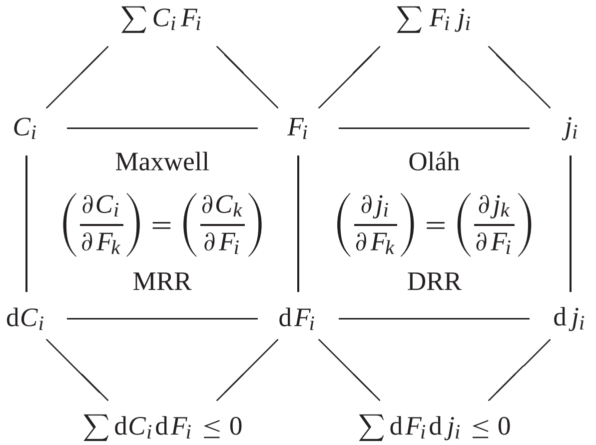
The second differential is the following scalar quantity:

$$\mathrm{d}^2 Z \equiv \sum_i \mathrm{d} j_i \cdot \mathrm{d}F_i \le 0. \tag{103}$$

$\mathrm{d}^2 Z$ is always non-positive. This property is equivalent to the statement that the matrix of Λ_{ik} is negative definite, or that fluxes j_i are dominant *monotonic* functions of the potentials F_k.

$$\mathrm{d}^2 Z = \sum_i \sum_k \mathrm{d}F_i \cdot \Lambda_{ik} \cdot \mathrm{d}F_k. \tag{104}$$

This law is part of the Second Law, a dynamic stability of real systems.



C_i	F_i	j_i
U	$1/T$	j_U
C_k	$-\mu_k/T$	j_k
etc.	etc.	etc.

(II. Law)

Fig. 11. Static and dynamic relations of equilibrium state

Conclusions

Analysis of basic properties and behaviour of equilibrium thermodynamic systems has led to a number of important perceptions.

1. Three groups of quantities take part in establishing and governing equilibrium states:
   a. Conservative extensive additive quantities (and their densities, C_i).
   b. Absolute processes inside and between equilibrium phases, j_i.
   c. The group of the (independent) potentials F_i.
2. Three phase spaces:
   a. Density (Gibbs) space.
      The principal quantity is the entropy density S/V.
   b. Potential (Gibbs–Duhem) space.
      The principal quantity is: $-P/T$.
   c. The dynamic space of the absolute process rates.
      The principal quantity is the Dynamic Potential.
3. Three groups of state equations can be introduced:
   a. EOS: canonical forms of the equations $C(F)$.
   b. EOR: canonical forms of the equations $j(F)$.
   c. Equations of MA type: equations $j(C)$.
4. Two cross reciprocities are observed and proved:
   a. Maxwell's Reciprocity Relations (MRR) of the EOS.
   b. Oláh's Dynamic Reciprocity Relations (DRR) of the EOR.
5. Three reverse laws of the process relations:

   a. The Law of Detailed Balance (DB): equilibration of j's at equilibrium.
   b. The General Reverse Symmetry (RS) of the $j(F)$ relations.
   c. The reverse symmetry of the rate constants of the $j(F)$ rate equations.

6. Irreversibility built into the equilibrium relationships (inequalities, Second Law):
   a. Negativity of the second differential of the entropy density.
   b. Negativity of the second differential of the Dynamic Potential.

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