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Objekttyp: **Article**

Zeitschrift: **Helvetica Physica Acta**

Band (Jahr): **36 (1963)**

Heft VII

PDF erstellt am: **11.07.2024**

Persistenter Link: https://doi.org/10.5169/seals-113405

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Non-relativistic Thermodynamics IV (Sign Questions and Onsager Symmetry Relations in Phenomenological Theory)

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Abstract. The signs of thermodynamical state functions are defined in terms of the *sign of absolute temperature* T. 1) The *2nd Law's principle of evolution* determines the signs of the (*symmetrised*) *phenomenological coefficients* $L_{(\alpha\beta)}$. 2) The *2nd Law's principle of* (*cinetic*) *equilibrium* determines the signs of *the remaining state functions* (*mass densities of the chemical components A* in *a C*(>1)-*component fluid*, its *elastic modulus*, and other state functions appearing in the *coupled linearised equations of motion*). These sign conditions show that the solutions of these equations are damped waves existing only in the future. It is remarkable, that the phenomenological coefficients satisfy *Onsager's symmetry relation* $L_{AB} = L_{BA}$ for the diffusion of substances $A\ B \ldots = 12 \ldots C$, *if both principles are applied.*

§ 1. Introduction and Conclusion

The aim of this article, in which the author wishes to express his admiration to Prof. W. HEITLER's work, is twofold: It is a complement to a previous paper on the *questions of sign of certain local thermodynamical state functions* $f[s \ldots] = f(\vec{x}\ t)$ *in r.* (= *relativistic*) *phenomenological theory* of a *one component fluid* III[4]). We investigate the analogous questions for the n.r. (= non-relativistic) case, postulating *Galilei-covariance*, for a fluid composed *of C chemical components*, numbered by $A\ B \ldots = 12 \ldots C$. The symbols $A\ B \ldots$ are also used to denote the *unites of mass* (A = mass of the mole of A). We deduce a the *symmetry condition on the Onsager phenomenological coefficients* L_{AB} defined as linear relations between *the densities of conduction-(diffusion-) currents* $\vec{j}_A\ (\vec{x}\ t)$ of A (including the *conductive entropy* (S) –*flow* $\vec{j}_S\ (\vec{x}\ t)$) and the «*thermodynamical forces*» $-\overrightarrow{\text{grad}}\ T\ (\vec{x}\ t)$ and $-\overrightarrow{\text{grad}}\ \mu_A\ (\vec{x}\ t)$ *):

$$\vec{j}_S = -L_{SS}\ \overrightarrow{\text{grad}}\ T - \Sigma_B\ L_{SB}\ \overrightarrow{\text{grad}}\ \mu_B\,, \qquad (1.1_S)$$

$$\vec{j}_A = -L_{AS}\ \overrightarrow{\text{grad}}\ T - \Sigma_B\ L_{AB}\ \overrightarrow{\text{grad}}\ \mu_B\,. \qquad (1.1_A)$$

Among the *local state variables* $s\ (\vec{x}\ t)$ and $n_A\ (\vec{x}\ t)$ (*densities of entropy* S and of *quantity* N_A of component A) figures, in the non static case the $d(=3)$ *velocity components of the fluid* $v^i\ (\vec{x}\ t)$ ($\vec{v} = \{v^i\}$; $\vec{x} = \{x^i\}$; $i\ k \ldots = 12 \ldots d$; $d = 3$). In order

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*) T and μ_A are the local absolute temperature and the local chemical potential of component A.

to avoid additional local state variables, $\vec{v}(\vec{x})$ has to be defined as the (*local*) *velocity of the centre of mass in a volume element* $dV(\vec{x}) = \mathfrak{g}\, dx^1\, dx^2 \dots dx^d$*).

This implies a *first restriction* (see (2.27)) on the $L_{A\,B}$'s.

$$\Sigma_A\, A\, \vec{j}_A\, (\vec{x}\, t) = 0\,, \tag{1.2}$$

$$\boxed{\Sigma_A\, A\, L_{A\,B}\, (\vec{x}\, t) = 0\,.} \tag{1.3}$$

From the *2nd law* (*principle of evolution*: $\dot{S}(t) \geq 0$ for a closed system) follows that the coefficients in (1.1)

$$\left\{\begin{matrix} T^{-1}\, L_{S\,S}\,, & T^{-1}\, L_{(S\,B)} \\ T^{-1}\, L_{(A\,S)}\,, & T^{-1}\, L_{(A\,B)} \end{matrix}\right\} (\vec{x}\, t) \geq 0 \qquad (1.4)\,^{***)}$$

forms *a non-negative quadratic form.*

The *2nd law's principle of equilibrium* ($S =$ maximum, for a closed system in cinetic equilibrium) leads to a relation symmetric to (1.3)

$$\boxed{\Sigma_B\, L_{A\,B}\, (\vec{x}\, t)\, B = 0\,.} \tag{1.5}$$

In phenomenological theory, the masses $A\ B \dots C$ are arbitrary constante. Therefore, the *Onsager relations*

$$\boxed{L_{A\,B}\, (\vec{x}\, t) = L_{B\,A}\, (\dots) = L_{(A\,B)}\, (\vec{x}\, t)} \qquad (1.6)\,^{**)}$$

follow from *phenomenological theory.*

(The Onsager relations are $L_{\alpha\beta} = L_{\beta\alpha} = L_{(\alpha\beta)}$***) (if no magnetic field is present) *for all phenomenological coefficients*, relating «*thermodynamical currents*» J_α to «*thermodynamical forces*» X_α ($J_\alpha = \Sigma_\beta L_{\alpha\beta} X_\beta$). They follow only from *statistical thermodynamics* (see 1) 2) 3)). *However, the Onsager relations for diffusion of substance are already consequences of phenomenological theory.*

Further consequences of the *principle of evolution* apply to the *transversal and longitudinal viscosities* η and ξ

$$(T^{-1}\, \eta)\, (\vec{x}\, t) \geq 0\,; \quad (T^{-1}\, \xi)\, (\vec{x}\, t) \geq 0 \tag{1.7}$$

and to the bilinear form formed from *longitudinal viscosity* $\xi = d^{-2}\, L_{00}$ and the Onsager coefficients of *local reaction rates* $L_{0\,a}$, L_{a0} and $L_{a\,b}$ refering to the r possible chemical reactions $a\ b \dots = 12 \dots r$ given by the stochiometric coefficients $\nu_{a\,A}$ (= pos. and neg. integers):

$$\boxed{\Sigma_A\, \nu_{a\,A}\, A = 0\,,} \tag{1.8}$$

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*) $\mathfrak{g}$ is a constant scalar density ($= |\det (g_{..})|$, if a metric g_{ik} is assumed (see § 2)).

**) From (1.3) and (1.5) follows, for arbitrary mass values $A\ B \dots C$: $L_{A\,B} = \lambda\, L_{B\,A}$. This can be seen by the following argument: Given the $L_{A\,B}$'s, (1.3) determines the *unknown* A's up to a common factor λ_1 ($A \to \lambda_1\, A$, $B \to \lambda_1\, B$, ...). The A's (or B's) must also satisfy (1.5). Therefore we must have $L_{A\,B} = \lambda_2\, L_{B\,A}$. Applied to $L_{A\,A}$, λ_2 must be $= 1$. Thus (1.6) follows.

***) Indices in round brackets $(A\ B)$, $(i\ k)$, ... imply *symmetry*. Square brackets $[A\ B]$, $[ik]$, ... *signify antisymmetry*.

$$\begin{vmatrix} T^{-1} L_{00}, & T^{-1} L_{(0b)} \\ T^{-1} L_{(a0)}, & T^{-1} L_{(ab)} \end{vmatrix} (\vec{x}\, t) \geq 0 . \qquad (1.9)^{***)}$$

(The index $_0$ applies to the longitudinal viscosity).

The principle of equilibrium (fluid with constant translational and angular velocity) requires conditions on *mass density m and* metric g_{ik}

$$\{(T^{-1} m)\,(\vec{x}\, t)\, g_{ik}\} = \{(T^{-1} \Sigma_A\, A\, n_A\, (\vec{x}\, t)\, g_{ik}\} \geq 0 , \qquad (1.10)$$

on the *elastic modulus*

$$a\,[s \ldots n_A \ldots] = (s^2\, u_{ss} + 2\, s\, \Sigma_A\, n_A\, u_{s n_A} + \Sigma_A\, \Sigma_B\, n_A\, n_B\, u_{n_A n_B}) , \qquad (1.11)^{*)}$$

$$(T^{-1}\, a)\,(\vec{x}\, t) \geq 0 , \qquad (1.12)$$

on the *heat capucity per unit volume c*

$$c^{-1}\,(\vec{x}\, t) = (T^{-1}\, T_s)\,[s \ldots n_A \ldots] \geq 0 \qquad (1.13)^{*)}$$

and on other *bilinear forms* (see (3.12)) of *local state variables.*

There is no loss of generality, if the *metric is assumed positive* **) (1.10), and the A's are assumed positive masses. Thus mass, elastic modulus, viscosities and all other state functions (the $L_{\alpha\beta}$'s) have a well defined sign in terms of T. This leads to coupled equations of motion for

$$\partial_t s\,(\vec{x}\, t) , \quad \partial_t n_A\,(\vec{x}\, t) \text{ and } \partial_t v^i\,(\vec{x}\, t) \qquad \text{(see III}^{4)\,5)}\text{)} ,$$

which lead, *in the linear approximation, to damped waves, which exist only for* t ≥ 0 (if the initial state is given for $t = 0$).

We apologize for deducing several well known results (see [2]). However, making extensive use of *Galilei-covariance,* we prepare the way for an article *on the r. C* (>1)-*component fluid,* based on *Lorentz-covariance,* where several difficulties occur, which we failed to see, when writing I[4].

§ 2. The Equations of Motion
(Continuity Eqs. Following from the 1st and 2nd Law)

We denote by V the volume, the interior part of space $\vec{x}$ inside the *time dependent closed surface* $C\,(\vec{y}\, t) = 0$ and by $d\sigma_i\,(\vec{y}\, t)$ the covariant surface element ($= \pm \mathfrak{g}\, dy^1 \ldots dy^{i-1}\, dy^{i+1} \ldots dy^d$).

A capital letter $F(t)$ is an *extensive quantity* (with the exception of $T\,(\vec{x}\, t)$) and $f\,(\vec{x}\, t) = f\,[s\,(\vec{x}\, t), \ldots]$ the *corresponding density* (= *local state function*). The time variation of $F(t) = \int_V (dV f)\,(\vec{x}\, t)$ is:

$$\dot{F}(t) = \int_V (dV\, \partial_t f)\,(\vec{x}\, t) + \oint_V (d\sigma_i\, v^i\, f)\,(\vec{y}\, t) , \qquad (2.1)$$

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*) $u_s\,[s \ldots n_A \ldots] = \partial u\,[s \ldots n_A \ldots]/\partial s;\ u_{ss} = \ldots;\ u_{s n_A}\,[\ldots] = \partial^2 u\,[\ldots]/\partial s\, \partial n_A;\ u_{n_A n_B} = \ldots$

**) As g_{ik} is constant, we may use *euclidian metric* $g_{ik} = \delta^i_k$.

***) See eq (2.46).

$v^i(\vec y\; t)$ is the velocity of the surface $C(\vec y\; t) = 0$. The *cause of this variation* is due 1) to a source *density* $\varrho_F(\vec x\; t)$ and 2) to an *influx* $-j^i_F(\vec y\; t)$ through $C(\ldots) = 0$:

$$\boxed{\dot F(t) = \int_V (dV\, \varrho_F)(\vec x\; t) - \oint_V (d\sigma_i\, j^i_F)(\vec y\; t)\,.} \qquad (2.2)$$

Assuming these two relations for all possible $C(\ldots) = 0$'s Gauss's theorem leads to the *inhomogenous continuity eq.*:

$$\boxed{(\partial_t f + \partial_k(v^k f + j^k_F))(\vec x\; t) = \varrho_F(\vec x\; t)\,.} \qquad (2.3)$$

The *current density of* F is separated in a *convective* $v^k f$ and a *conductive* (= *diffusion*) *part* j^k_F.

The *1st law* expresses *the conservation of energy* H, *momentum* Π_i and of the C *quantities of substance* N_A. In the continuity equation for H, we separate the conductive flow in *heat flow* q^i, *flow of work* a^i and *flow of chemical energy* c^i

$$\boxed{(\partial_t h + \partial_k(v^k h + q^k + a^k + c^k))(\vec x\; t) = \varrho_H(\vec x\; t) = (v^i k_i)(\vec x\; t)\,,} \qquad (2.9H)$$

where $k_i(\vec x\; t)$ is the *density of (external) volume force.* For Π_i, we write $j^k_{\Pi_i} = -\tau^k{}_i$ (= $-$*stress tensor*)

$$\boxed{(\partial_t \pi_i + \partial_k(v^k \pi_i - \tau^k{}_i))(\vec x\; t) = k_i(\vec x\; t)} \qquad (2.9\Pi_i)$$

and for N_A

$$\boxed{(\partial_t n_A + \partial_k(v^k n_A + j^k_A))(\vec x\; t) = \varrho_A(\vec x\; t) = \Sigma_a\, \nu_{aA}\, \omega_a(\vec x\; t)\,,} \qquad (2.9N_A)$$

where $\omega_a(\vec x\; t)$ is the *local reaction rate* of the a^{th} reaction (1.7). (2.9Π_i) is connected with the *homogeneity of space* $\{x^i\}$. If space is *isotropic* (metric $x_i = g_{ik}\, x^k$, g_{ik} = const.), the *1st law contains the conservation of angular momentum* $M_{ik} = M_{[ik]} = \int dV\,(x_i \pi_k - x_k \pi_i)$:

$$\boxed{\begin{aligned}&(\partial_t(x_i \pi_k - x_k \pi_i) + \partial_l(v^l (x_i \pi_k - x_k \pi_i)\\ &\qquad - (x_i \tau^l{}_k - x_k \tau^l{}_i)))(\vec x\; t) = (x_i k_k - x_k k_i)(\vec x\; t)\,.\end{aligned}} \qquad (2.9M_{ik})$$

(2.9Π_i) and (2.9M_{ik}) imply the symmetry ($\partial_i x^k = \delta^k_i$)

$$\boxed{(v_i \pi_k - \tau_{ik})(\vec x\; t) = (v_k \pi_i - \tau_{ki})(\vec x\; t)\,.} \qquad (2.10)$$

The *integral forms of the 1st law* (2.2) are

$$\left.\begin{aligned}\dot H(t) &= P_Q(t) + P_A(t) + P_C(t)\\ &= \Big(-\oint_V (d\sigma_i\, q^i)(\vec y\; t)\Big) + \Big(\int_V (dV\, k_i\, v^i)(\vec x\; t) + \oint_V (d\sigma_k\, \tau^k{}_i\, v^i)(\vec y\; t)\Big)\\ &\quad + \Big(-\oint_V (d\sigma_i\, c^i)(\vec y\; t)\Big),\end{aligned}\right| \qquad (2.11H)$$

$$\dot{\varPi}_i(t) = K_i(t) = \int\limits_{V} (dV\ k_i)\ (\vec{x}\ t) + \oint\limits_{V} (d\sigma_k\ \tau^k{}_i)\ (\vec{y}\ t)\,, \tag{2.11$\varPi_i$}$$

$$\dot{N}_A(t) = \int\limits_{\dot{V}} (dV\ \varrho_A)\ (\vec{x}\ t) - \oint\limits_{\dot{V}} (d\sigma_i\ j^i_A)\ (\vec{y}\ t)\,, \tag{2.11N_A}$$

$$\left.\begin{aligned} \dot{M}_{ik}(t) &= D_{ik}(t)\,, \\ &= \int\limits_{V} \big(dV\ (x_i\ k_k - x_k\ k_i)\big)\ (\vec{x}\ t) + \oint\limits_{V} \big(d\sigma_l\ (y_i\ \tau^l{}_k - \dot{y}_k\ \tau^l{}_i)\big)\ (\vec{y}\ t)\,, \end{aligned}\right\} \tag{2.11M_{ik}}$$

where P_Q etc. are the *powers of heat* Q, *work* A and *chemical energy* C. K_i and $D_{ik} = D_{[ik]}$ are the *total force* and *its total momentum.*

The *2nd law* states *the principle of evolution* for the entropy S. In its equation of continuity

$$\boxed{\big(\partial_t s + \partial_k(v^k\ s + j^k_S)\big)\ (\vec{x}\ t) = i\ (\vec{x}\ t) \geq 0\,,} \tag{2.12}$$

the source density $i\ (\vec{x}\ t)$ (= *density of irreversibility*) is non negative. The integral form is

$$\dot{S}(t) = \dot{S}^{(interior)}(t) + \dot{S}^{(exterior)}(t) = \int\limits_{\dot{V}} (dV\ i)\ (\vec{x}\ t) - \oint\limits_{\dot{V}} (d\sigma_k\ j^k_S)\ (\vec{y}\ t)\,, \tag{2.13) *}$$

with $\dot{S}^{(interior)} \geq 0$.

We add now *Newton's axiom,* defining *mass density* $m\ (\vec{x}\ t)$, in the form

$$\boxed{\pi_i\ (\vec{x}\ t) = m\ (\vec{x}\ t)\ v_i\ (\vec{x}\ t)\,,} \tag{2.14}$$

which implies the metric g_{ik}. The continuity equation (2.9$\varPi_i$) takes the form

$$\big(\big(v_i\ (\partial_t m + \partial_k(v^k\ m)\big) + m\ \dot{v}_i - \partial_k\ \tau^k{}_i\big)\ (\vec{x}\ t) = k_i\ (\vec{x}\ t)\,, \tag{2.15}$$

where $\dot{v}_i$ is the *substantial acceleration,* defined as the *substantial time derivative of any local function* $f\ (x\ t)$:

$$\boxed{\dot{f}\ (\vec{x}\ t) \equiv (\partial_t f + v^k\ \partial_k\ f)\ (\vec{x}\ t)\,.} \tag{2.16}$$

We remark that *any continuity* eq. (2.3) may be written as

$$\boxed{(\dot{f} + f\ \partial_k v^k + \partial_k j^k_F)\ (\vec{x}\ t) = \varrho_F\ (\vec{x}\ t)\,.} \tag{2.17}$$

We now turn to *Galilei-covariance.* The Galilei transformation

$$'x^i = x^i - v^i_0\ t\,, \quad 't = t + t_0\,, \tag{2.18}$$

(with constants v^i_0 and t_0) defines *Galilei-covariant tensors*

$$\boxed{'f^{ik\ldots}{}_{lm\ldots}\ ('\vec{x}\ 't) = f^{ik\ldots}{}_{lm\ldots}\ (x\ t)\,.} \tag{2.19}$$

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*) On account of (2.39) we have

$$\dot{S}(t) \geqslant - \oint\limits_{\dot{V}} (d\sigma_i\ T^{-1}\ q^i)\ (\vec{y}\ t)\,. \tag{2.13 *}$$

The velocity field $'v^i\,('\vec{x}\,'t) = v^i\,(\vec{x}\,t) - v_0^i$ is *not covariant*. However $\dot{v}^i$, $\partial_i v^k$ and $\partial_k v^k = \operatorname{div} \vec{v}$ are covariant. The same is true for $\dot{f}^{ik\dots}{}_{lm\dots}$, defined by (2.16), if $f^{ik\dots}{}_{lm\dots}$ is Galilei-covariant. Thus, if $\tau^k{}_i$ and k_i in (2.15) are Galilei-covariant, the *strong continuity eq. for mass* $M = \int_V (dV\,m)\,(\vec{x}\,t)$ holds:

$$\boxed{j^i_M = 0\,, \quad \varrho_M = 0\,, \quad \big(\partial_t m + \partial_k (v^k\,m)\big)\,(\vec{x}\,t) = 0\,,} \tag{2.20}$$

$$\boxed{\dot{M}(t) = 0\,,} \tag{2.21}$$

expressing the *strong conservation of mass M*. The equations of motion (2.20) and *Newton's law*

$$\boxed{\begin{aligned} (m\,\dot{v}_i)\,(\vec{x}\,t) &= \big(m\,(\partial_t v_i + v^k\,\partial_k\,v_i)\big)\,(\vec{x}\,t) \\ &= (\partial_k \tau^k{}_i + k_i)\,(\vec{x}\,t) \end{aligned}} \tag{2.22}$$

replace $(2.9\Pi_i)$.

If we chose as *independent local state variables, the* $d + 1 + C$ *variables* $\{v_i,\, s,\, n_A\}\,(\vec{x}\,t)$, we have to satisfy the $d + 1 + C + 2$ eqs. of motion: (2.22) for $\partial_t v_i$, (2.12) for $\partial_t s$, $(2.9N_A)$ for $\partial_t n_A$, $(2.9H)$ for $\partial_t h$, and (2.20) for $\partial_t m$. This implies that $m = m\,[\dots v_i \dots s \dots n_A \dots]$ and $h = h\,[\dots v_i \dots s \dots n_A \dots]$ are *given state functions*: Their 2 eqs. of motion must be *consequences* of the $d + 1 + C$ eqs. of motion for the independent variables $\partial_t v_i$, $\partial_t s$ and $\partial_t n_A$. Galilei-covariance for m reduces m to $m\,[s \dots n_A \dots]$. The 2 eqs. for $\partial_t m$ and $\partial_t h$ lead to 2 different expressions for the Galilei-covariant entropy source $i\,(\vec{x}\,t)$. As the form $i\,(\vec{x}\,t)$ resulting from $\partial_t m$ (2.20) can not be made non negative, a simple consideration leads to the result that the derivatives $\partial/\partial n_A$ of m:

$$m_{v^2}\,[\dots] = 0\,; \quad m_{n_A}\,[\dots n_A \dots] = A\,; \quad m_s\,[\dots] = 0\,, \tag{2.23}$$

must be C constants: $A\;B \dots C$, the molar masses. Thus we have

$$m\,[\dots n_A \dots] = \Sigma_A\,A\,n_A\,(\vec{x}\,t)\,. \tag{2.24}$$

No constant of integration can appear, on account of (2.20). However, $(2.9N_A)$ implies

$$\varrho_M = \Sigma_A\,A\,\varrho_A\,(\vec{x}\,t) = 0\,, \tag{2.25}$$

which combined with the 2nd eq. $(2.9N_A)$ leads to *Lavoisier's law* (1.8) stating the *conservation of mass in every chemical reaction a b … r*[*]. The condition $\vec{j}_M = 0$ (2.20) implies

$$(\vec{v}\,m)\,(\vec{x}\,t) = \Sigma_A\,A\,(n_A\,\vec{v} + \vec{j}_A)\,(\vec{x}\,t) \equiv \Sigma_A\,A\,(n_A\,\vec{v}_A)\,(\vec{x}\,t)\,, \tag{2.27}$$

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[*] Lavoisier's law is thus a *consequence of Galilei-covariance* in n.r. theory. It is interesting to note that no corresponding conservation law holds in r. theory (see III[4]). In order to obtain correspondance, continuity eqs. for

$$n_A\ (\rightarrow j^\alpha_A(x)\,;\ x = \{x^\alpha\}\,;\ \alpha\,\beta \dots = 12 \dots n\,;\ n = d + 1)$$

must be postulated. This is a further proof *that Galilei-transformations are not the limit of Lorentz-transformations*.

where $\vec{v}_A\,(\vec{x}\,t)$ is the velocity of component A. (2.24) and (2.27) define $\vec{v}\,(\vec{x}\,t)$ as the velocity of the local centre of mass. (1.2) and (1.3) are its consequences.

We now consider $\partial_t h$ (2.9H), using the $d+1+C$ eqs. of motion (2.22), (2.12) and (2.9N_A):

$$\left.\begin{aligned} \partial_t h &= h^i\,\partial_t v_i + h_s\,\partial_t\,s + h_{n_A}\,\partial_t n_A\,, \\ &= -\,\partial_k(v^k\,h + p\,v^k + h_s\,j_S^k + \Sigma_A\,h_{n_A}\,j_A^k) + h^i\,m^{-1}\,k_i \\ &\quad + v^i\,(s\,\partial_i h_s + \Sigma_A\,n_A\,\partial_i h_{n_A} - h^k\,\partial_i v_k) + h^i\,m^{-1}\,\partial_k \tau^k{}_i \\ &\quad + (h_s\,i + j_S^i\,\partial_i h_s + \Sigma_A\,j_A^i\,\partial_i h_{n_A} + \Sigma_A\,h_{n_A}\,\varrho_A)\,, \end{aligned}\right\} \tag{2.28}$$

with the abreviations $h^i = (\partial h\,[\ldots v_i \ldots s \ldots n_A \ldots]/\partial v_i)\,(\vec{x}\,t)$ and

$$p\,[\ldots v_i \ldots s \ldots n_A \ldots] = (s\,h_s + \Sigma_A\,n_A\,h_{n_A} - h)\,(\vec{x}\,t)\,. \tag{2.29}$$

The 2nd member of (2.28) must be transformed in such a way as giving rise to the divergence $\partial_k(v^k\,h + \ldots)$ in (2.9H) plus the source term $\varrho_H = v^i\,k_i$. But, this 2nd term of (2.9H) appears only, if we identify in the 2nd term of (2.28) with ϱ_H:

$$(h^i\,m^{-1} = v^i)\,(\vec{x}\,t)\,, \tag{2.30}$$

from which results, by integration

$$h\,[\ldots v_i \ldots s \ldots n_A \ldots] = \frac{1}{2}\,m\,[\ldots n_A \ldots]\,v^2 + u\,[s \ldots n_A \ldots]\,. \tag{2.31 *)}$$

The integration «constant» $u\,[\ldots]$ being the *density of interior energy*

$$U = \int\limits_{\vec{V}} (dV\,u)\,(\vec{x}\,t)\,.$$

Furthermore (2.29) becomes the *Galilei-invariant scalar pression*

$$p\,[s \ldots n_A \ldots] = (s\,u_s + \Sigma_A\,n_A\,u_{n_A} - u)\,(\vec{x}\,t)\,. \tag{2.32}$$

The factor of v^i in the 3rd term is its gradiant

$$\left.\begin{aligned} \partial_i p\,(\vec{x}\,t) &= (s\,\partial_i h_s + \Sigma_A\,n_A\,\partial_i\,h_{n_A} - h^k\,\partial_i v_k)\,[\ldots v_i \ldots s \ldots n_A \ldots]\,, \\ &= (s\,\partial_i u_s + \Sigma_A\,n_A\,\partial_i u_A)\,[s \ldots n_A \ldots] \end{aligned}\right\} \tag{2.33}$$

the second equality deriving from (2.31) and (2.23). It is function of the scalar state variables $[s \ldots n_A \ldots]$ and their 1st space derivatives $[\partial_i s, \ldots\,\partial_i n_A \ldots]$. Decomposing the stress tensor τ^{ik} in an elastic (e) and a frictional (f) part

$$\tau^{i\,k} = \tau^{i\,k(e)} + \tau^{i\,k(f)} = -\,g^{i\,k}\,p + \tau^{i\,k(f)}\,, \tag{2.34}$$

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*) It is remarkable that in the cinetic energy density term, which one would expect to have the form

$$\Sigma_A\,\frac{1}{2}\,A\,n_A\,v_A^2 = \frac{1}{2}\,m\,v^2 + \Sigma_A\,A\,n_A\,(\vec{v}_A - \vec{v},\,\vec{v}) + \frac{1}{2}\,\Sigma_A\,A\,n_A\,|\,\vec{v}_A - \vec{v}\,|^2$$

(the 2nd term disappears on account of (2.27)), the Galilei-covariant last term $(= 1/2\,\Sigma\,A\,n_A{}^{-1}\,|\,\vec{j}_A\,|^2)$ is missing. This is due to the fact, that we do not consider the $\vec{j}_A$'s (or $\vec{v}_A$'s) as being among the $d+1+C$ state variables. Physically, it means *neglecting the cinetic energy of diffusion* (see [2])).

the 2nd and 3rd term in (2.28) can, due to (2.30), be written as

$$v^i\,(\partial_i p + \partial_k \tau^k{}_i) = -\,\partial_k\,(-\tau^{k(f)}_i\,v^i) - v_{ik}\,\tau^{i\,k(f)}\,, \tag{2.35}$$

where

$$2\,v_{ik}\,(\vec{x}\,t) = (\partial_i v_k + \partial_k v_i)\,(\vec{x}\,t) = 2\,v_{(i\,k)} \tag{2.36}$$

is the symmetric, *Galilei-covariant*, velocity gradient. Its appearence is due to the symmetry

$$\boxed{\tau^{i\,k} = \tau^{(i\,k)}}$$

resulting from *conservation of angular momentum* (2.10) and Newton's axiom (2.14).

The first term of (2.35) may be combined with $p\,v^k$ in the divergence in (2.28) giving rise to the *flow of work*

$$\boxed{a^k = -\,\tau^k{}_i\,v^i\,.} \tag{2.38}$$

The other terms (aside from $h\,v^k$) in this divergence are the *heat flow*

$$\boxed{q^k = h_s\,j_S^k = u_s\,j_S^k \equiv T\,j_S^k} \tag{2.39}$$

and the *flow of chemical energy*

$$\boxed{c^k = \Sigma_A\,h_{n_A}\,j_A^k = \Sigma_A\,u_{n_A}\,j_A^k \equiv \Sigma_A\,\mu_A\,j_A^k\,,} \tag{2.40 *)}$$

where the *absolute temperature* T and the C *chemical potentials* μ_A are the local state functions

$$\boxed{T\,(\vec{x}\,t) = u_s\,[s\,\ldots\,n_A\,\ldots]\,;\quad \mu_A\,(\vec{x}\,t) = u_{n_A}\,[s\,\ldots\,n_A\,\ldots]\,.} \tag{2.41}$$

The 2nd term in (2.35) adds to the last term of (2.28) defining the density of irreversibility as

$$\boxed{\begin{aligned} i\,(\vec{x}\,t) = T^{-1}\,(\vec{x}\,t)\,\Big[\Big(&\Sigma_a\,\omega_a\,\mu_a + \frac{1}{d}\,\tau_l^{l(f)}\,v_k^k\Big) \\ &+ \big(j_S^i\,(-\,\partial_i T) + \Sigma_A\,j_A^i\,(-\,\partial_i\mu_A)\big) + \big(\tau^{i\,k(f)\,(0)}\,v_{ik}^{(0)}\big)\Big] \geq 0\,, \end{aligned}} \tag{2.42}$$

where

$$\boxed{\mu_a = -\,\Sigma_A\,\nu_{a\,A}\,\mu_A\,;\quad a\,b\,\ldots = 1, 2\,\ldots\,r} \tag{2.43}$$

is the «thermodynamical force» of reaction a. $\tau^{i\,k(0)}$ and $v_{ik}^{(0)}$ are the *trace-less irreducible parts of symmetric tensors*:

$$v_{ik}^{(0)} = v_{ik} - \frac{1}{d}\,g_{ik}\,v_l^l\,. \tag{2.44}$$

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*) $\vec{q}$ and $\vec{c}$ are *Galilei-covariant vectors*, the dependence on v^2 in $h_{n_A} = (1/2)\,A\,v^2 + u_{n_A}$ drops out in the sum on account of (1.2).

Thus $(T\, i)\, (\vec{x}\, t)$ is a sum of products of $(r + 1) + (1 + C) + 1$ unknown «*thermodynamical currents*» J_α $(\alpha\, \beta \ldots = 12 \ldots (r + C + 3))$ with the corresponding «*thermodynamical forces*» X_α, separating into scalars $(\omega_a, \tau_l^{l(f)})$, vectors $(\dot{j}_S^i, \dot{j}_A^i)$ and an irreducible tensor $\tau^{i\,k(f)\,(0)}$. Furthermore, $(T\, i)\, (\vec{x}\, t)$ must be a Galilei-covariant scalar. The «forces» X_α $(= (\mu_a, d^{-1}\, v_k^k), (-\partial_i T, -\partial_i \mu_A)$ and $v_{ik}^{(0)})$ being Galilei-covariant, the Onsager coefficients $L_{\alpha\beta}\, (\vec{x}\, t)$ in $J_\alpha = \Sigma_\beta\, L_{\alpha\beta}\, X_\beta$ must be Galilei-covariant state functions, satisfying

$$\{T^{-1}\, L_{(\alpha\,\beta)}\}\, [s \ldots n_A \ldots] \geq 0\,, \tag{2.45}$$

which may however depend on space-derivatives $\partial^n_{i_1 \ldots i_n} s\, (\vec{x}\, t) \ldots$ If we neglect these space derivatives, i.e. if we assume them to be *local state variables*, the $L_{\alpha\beta}$'s must be scalars. This leads to

$$\tau_l^{l(f)} = L_{00}\, \frac{1}{d}\, v_l^l + \Sigma_b\, L_{0\,b}\, \mu_b\,, \qquad \omega_a = L_{a\,0}\, \frac{1}{d}\, v_l^l + \Sigma_b\, L_{a\,b}\, \mu_b \tag{2.46}$$

for the scalar «currents», to (1.1) for the vector «currents» and to

$$\tau^{i\,k(f)\,(0)} = 2\, \eta\, v^{i\,k(0)} \tag{2.47}$$

for the tensor «current». The signes are defined in terms of $T\, (\vec{x}\, t)$ by (1.9), (1.4) and (1.7).

§ 3. The State of Cinetical Equilibrium

The most general equilibrium is given by the *maximum of the entropy-functional* $S\, [s\, (\,)] = \int (dV\, s)\, (\vec{x})$, with the *constraints on the functionals of the 1st law*:

$$H\, [\ldots] = H'\,; \quad \Pi_i\, [\ldots] = \Pi_i'\,; \quad M_{ik}\, [\ldots] = M_{ik}'\,.$$

If chemical reactions are possible, no constraints are imposed on the $C\; N_A\, [\ldots]$'s, but on the quantities of the I chemical elements $N_P\, [\ldots] = N'_P\, (P, Q \ldots = 12 \ldots I = H, D, He, \ldots, U, Pu, \ldots)$ (where $P, Q \ldots$ symbolise also *the masses of the atom-gram*). We have the relations

$$\Sigma_P\, \nu_{A\,P}\, P - A \equiv \Sigma_P\, \nu_{A\,P}\, P + \nu_{A\,A}\, A = 0 \tag{3.1A}$$

which apply also to the mass values and are the stochiometric relations (1.8) ($\nu_{A\,P} =$ pos. integers, $\nu_{A\,A} = -1$) for *complete dissociation* of A. Further we have evidently

$$N_P\, [\ldots n_A \ldots] = \Sigma_A\, \nu_{A\,P} \int (dV\, n_A)\, (\vec{x})\,. \tag{3.2}$$

The *necessary and sufficient condition for equilibrium*, is, as we have shown in III (annex)[4]:

$$\left.\begin{aligned} \Psi\, [\ldots v_i(\,) \ldots s(\,) \ldots n_A(\,) \ldots] &= \int (dV\, \psi\, [\ldots v_i \ldots s \ldots n_A \ldots])\, (\vec{x}) \\ &= \Big(S + \vartheta\, H - \zeta^i\, \Pi_i - \frac{1}{2}\, \omega^{i\,k}\, M_{ik} - \Sigma_P\, \beta_P\, N_P)\, [\ldots] = \text{maximum.} \end{aligned}\right\} \tag{3.3}$$

ϑ, ζ^i, $\omega^{ik} = \omega^{[ik]}$ and β_P are *Lagrange multiplyers. The 1st variation* $\delta^{(1)}\Psi\,[\ldots] = 0$ *is the extremum condition.* It yelds (see III[4])):

$$\psi^i(\vec{x}) = \vartheta\, m\, v^i - m\,(\zeta^i + x_k\,\omega^{ki}) \equiv 0\,, \tag{3.4^i}$$

$$\psi_s(\vec{x}) = 1 + \vartheta\, u_s = 1 + \vartheta\, T(\vec{x}) \equiv 0\,, \tag{3.4$_s$}$$

$$\psi_{n_A}(\vec{x}) = \vartheta \left(A\,\frac{v^2}{2} + u_{n_A}\right) - A\,(\zeta^i + x_k\,\omega^{ki})\,v_i - \Sigma_P\,\nu_{AP}\,\beta_P \equiv 0\,. \tag{3.4$_{n_A}$}$$

(3.4^i) implies a *translation + rotation with constant linear and angular velocity* of the fluid:

$$\vec{v}(\vec{x}) = (\vec{\zeta} + [\overset{\curvearrowright}{\omega} \wedge \vec{x}])\,\vartheta^{-1}\,. \tag{3.5}$$

(3.4$_s$) shows that $T(\vec{x}) = -\vartheta^{-1}$ is *independent of space.* (3.4$_{n_A}$) gives the chemical potentials the form

$$\mu_A(\vec{x}) = \mu_A(0) + \frac{1}{2}\,A\,v^2(\vec{x})\,, \tag{3.6}$$

$$\mu_A(0) = \Sigma_P\,\nu_{AP}\,\vartheta^{-1}\,\beta_P\,(\equiv \Sigma_P\,\nu_{AP}\,\mu_P(0))\,. \tag{3.7}$$

On account of (3.1), this implies *local chemical equilibrium with respect to total dissociation*

$$(\Sigma_P\,\nu_{AP}\,\mu_P + \nu_{AA}\,\mu_A)\,(\vec{x}) = 0\,. \tag{3.8A) *)$$

As all other r reactions a can be combined from the C reactions (3.1A) and (3.8A), chemical equilibrium is thus assured at every point $\vec{x}$, i.e. (2.43) gives

$$\mu_a(\vec{x}) = 0\,. \tag{3.9}$$

As from (3.5) follows $v_{ik}(x) = 0$, the irreversibility $i(\vec{x})$ (2.42) disappears for the scalar and tensorial terms.

We have now to *verify that the equations of motion* ((2.22), (2.9N_A) and (2.12) with $k_i(\vec{x}) = 0$) are satisfied. As $\tau^{ik(f)}$ disappears on account of $v_{ik} = 0$ and $\mu_a = 0$ ((2.46), (2.47)). (2.22) reduces to (on account of $T =$ const. (2.33), (2.41), (2.24) and (3.6)):

$$(m\,\dot{v}_i + \partial_i p)\,(x) = (m\,v^k\,\partial_k v_i + \Sigma_A\,n_A\,\partial_i\mu_A) = 2\,\Sigma_A\,A\,(n_A\,v^k\,v_{ki})\,(\vec{x}) = 0\,. \tag{3.10}$$

The Equations (2.12) for $\dot{s}$ and (2.9N_A) for $\dot{n}_A$, written in the Galilei-covariant form (2.7), are satisfied, if div $\vec{j}_S =$ div $\vec{j}_A = 0$: ϱ_A disappears on account of (2.46), because $v_l^l = \mu_a = 0$. Furthermore $i(\vec{x})$ vanishes now for all 3 terms. Thus, as T is constant, the condition div $\vec{j}_S =$ div $\vec{j}_A = 0$ implies

$$\Sigma_B\,L_{SB}\,B = 0 \tag{3.11}$$

and necessitates (1.5). (div $\overrightarrow{\text{grad}}\,\mu_B = B$ div $\overrightarrow{\text{grad}}\,v^2/2 \neq 0$).

Thus (2.12) and (2.9N_A) lead to

$$\dot{s}(\vec{x}) = 0\,; \quad \dot{n}_A(\vec{x}) = 0\,. \tag{3.12}$$

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*) On account of (2.25), which implies (1.8), where A are now the molar masses.

Or, substantial time derivatives $\dot{f}$ of scalar state functions disappear for (3.5). It is remarkable, that the eqs. of motion for a *one-component fluid* (in r. and n.r. (see III[4])) theory) *are identically satisfied*. For a $C(>1)$*-component fluid*, we have however *the restrictions* (1.5) *and* (3.11) *on the Onsager coefficients in n.r. theory**).

The 2nd variation $\delta^{(2)}\Psi\,[\ldots] \leq 0$ is a necessary condition (see III[4]), annex). It implies

$$\left\{\begin{matrix} \psi^{i\,k}, & \psi^{i}_{s}, & \psi^{i}_{n_B} \\ \psi^{k}_{s}, & \psi_{s\,s}, & \psi_{s_{n_B}} \\ \psi^{k}_{n_A}, & \psi_{n_A\,s}, & \psi_{n_A\,n_B} \end{matrix}\right\} (\vec{x}) \leq 0\,, \tag{3.12}$$

which implies (see (3.4))

$$\left\{-\psi^{i\,k} = -\vartheta\, m\, g^{i\,k} = \left(\frac{m}{T}\right)(\vec{x})\, g^{i\,k}\right\} \geq 0\,, \tag{3.13$^{i\,k}$}$$

$$-\psi_{s\,s} = -\vartheta\, u_{s\,s} = \left(\frac{T_s}{T}\right)[s \ldots n_A \ldots] = c^{-1}\,(\vec{x}) \geq 0\,, \tag{3.13$_{s\,s}$}$$

$$-\psi_{s\,n_A} = -\vartheta\, u_{s\,n_A} = \left(\frac{u_{s n_A}}{T}\right)(\vec{x})\,, \tag{3.13$_{s\,n_A}$}$$

$$\left\{-\psi_{n_A\,n_B} = -\vartheta\, u_{n_A\,n_B} = \left(\frac{u_{n_A\,n_B}}{T}\right)(\vec{x})\right\} \geq 0\,. \tag{3.13$_{n_A\,n_B}$}$$

(3.13) has for consequence that a) *the metric must be euclidien* $\{g^{ik}\} \geq 0$**) and that the *mass density and therefore* $A\; n_A(\vec{x}\;t)$ *have the sign of* T. (3.13$_{s\,s}$, $_{s\,n_A}$ and $_{n_A\,n_B}$) give *to the elastic modulus* (1.11) *the sign of* T.

The sign condition on the Onsager coefficients (2.45) resulting from *the 2nd law's principle of evolution* and on the $\psi^{\cdot\cdot}$,s (3.13) *from the 2nd law's principle of equilibrium* have as a consequence that the solution of the *linearised coupled equations* for $\dot{v}^i$, $\dot{s}$ and $\dot{n}_A$ ((2.22), (2.9 N_A) and (2.12)) are *damped waves existing only in the future* $t \geq 0$, if the *initial local states* are given for all $\vec{x}$ at $t =$ III[4])[5]).

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) We shall discuss the analogous conditions for a $C(>1)$-component fluid in r. theory* in a subsequent paper (V).

**) $\{g_{ik}\} \leqslant 0$ is of course also possible, if $(m/T)\,(\vec{x}) \leqslant 0$.