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RELATIVISTIC THERMODYNAMICS OF IRREVERSIBLE PROCESSES I

HEAT CONDUCTION, DIFFUSION, VISCOUS FLOW AND CHEMICAL REACTIONS; FORMAL PART

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Synopsis

The relativistic thermodynamics of irreversible processes is developed for an isotropic mixture in which heat conduction, diffusion, viscous flow, chemical reactions and their cross-phenomena may occur. The four-vectors, representing the relative flows of matter, are defined in such a way that, in the four-dimensional space-time continuum, they are perpendicular to the four-vector which represents the barycentric velocity. The entropy balance is derived from the fundamental relativistic macroscopic laws. If n is the number of chemical components, we find $n + 4$ relations among the $4n + 4$ phenomenological equations which we obtain for the relative flows of matter and the heat flow. Owing to these relations we retain just that number ($3n$) of independent equations which would be expected from physical considerations. It is shown that the Onsager relations are Lorentz invariant. A new cross-effect is found between diffusion and heat conduction, arising from a relativistic term in the force conjugate to the heat flow. It appears that due to this cross-effect the diffusion phenomena are influenced by the barycentric motion.

§ 1. *Introduction.* The purpose of this paper is to extend Eckart's theory [1]) of the relativistic thermodynamics of irreversible processes in a smiple fluid to a mixture of an arbitrary number of chemical components, and to derive physical results with the help of the Onsager relations. We shall assume that matter (rest mass) cannot change into other forms of energy, and we shall limit ourselves to the special theory of relativity. Further, we shall make the restrictions that there are no external forces depending on the velocity of matter, and that the medium is isotropic. We give the theory in four-dimensional tensor form, hence, the relativistic invariance is assured. We shall deal with the phenomena of diffusion, heat conduction, viscous flow and chemical reactions and with their cross-effects.

Having defined a barycentric velocity, the Lorentz frame in which this velocity vanishes will be called the barycentric Lorentz frame. As guiding principle we shall assume that in the barycentric Lorentz frame all equations have to correspond closely to the non-relativistic equations. Our method is analogous to Eckart's procedure (except in some points of interpretation) and is closely related to the non-relativistic one [2]).

The validity of the theory is limited by the condition that in the barycentric Lorentz frame the variations in temperature, pressure, etc. must be small over a distance comparable with the mean free path of the molecules. This state of affairs is analogous to the non-relativistic case [3]).

In §§ 2 and 3 we discuss some preliminaries needed in the development of the theory. In § 4 we introduce four fundamental laws. In the first place we have the momentum law and the balance equation for the energy. Since we assume that matter cannot change into other forms of energy we may also introduce a conservation law for total rest mass. As fourth fundamental equation we introduce the second law of thermodynamics (Gibbs relation). In § 5 we derive the first law of thermodynamics for the internal energy of the system, measured by an observer in the barycentric Lorentz frame, from the first three fundamental equations mentioned before. In § 6 we derive the relativistic analog of the entropy production, well-known from the non-relativistic theory. The phenomenological laws are formulated in § 7 and it is shown that the Onsager relations are invariant under Lorentz transformations. Eckart has found that acceleration of matter causes a heat flow and it will be shown that it also gives rise to a diffusion flow. This phenomenon resembles thermal diffusion because both are cross-effects of heat conduction and diffusion.

In a following paper we shall formulate the theory with the aid of three-dimensional vectors, by means of which concepts of physical interest will be introduced.

§ 2. *Flows of matter and related notions.* Before stating the fundamental equations, which we need for the calculation of the entropy production, we shall first introduce some useful notions. In § 3 we shall consider the energy-momentum tensor and some quantities which may be derived from this tensor, while in this section we shall deal with such notions as densities, concentrations and flows of matter, the barycentric Lorentz frame, the barycentric time derivative and an auxiliary tensor.

We assume a four-dimensional coordinate system (x_1, x_2, x_3, $x_4 = ict$), where x_1, x_2 and x_3 are the coordinates in ordinary space, c is the velocity of light and t is the time. By taking $x_4 = ict$, we have the metric tensor given by the Kronecker symbol and thus associated contravariant and covariant tensors become identical.

Furthermore, we shall assume that we have a mixture of n components. If $N^{(j)}$ is the number of atomic particles (electrons and atomic nuclei) of component j per unit volume (the volume being at rest with respect to the observer) and $M^{(j)}_{(0)(k)}$ is the rest mass of particle k if it is free (not bound in an atom, molecule or ion) we define as density of rest mass of component j the quantity $\varrho^{(j)} \equiv \Sigma_{k=1}^{N(j)} M^{(j)}_{(0)(k)}$. We can represent *the flow of matter* of component j, as is well-known, by a four-vector of which the components in space-time continuum are defined by

$$m_1^{(j)} \equiv \varrho^{(j)} v_1^{(j)};\ m_2^{(j)} \equiv \varrho^{(j)} v_2^{(j)};\ m_3^{(j)} \equiv \varrho^{(j)} v_3^{(j)};\ m_4^{(j)} \equiv ic\varrho^{(j)}.\ (j = 1, \ldots, n) \tag{2.1}$$

where $\mathbf{v}^{(j)}$ is the velocity of component j. Chemical components will always be denoted by a superscript and tensor components by a subscript.

The total density of rest mass is given by

$$\varrho \equiv \Sigma_{j=1}^{n} \varrho^{(j)}. \tag{2.2}$$

The specific volume is defined by

$$v \equiv \varrho^{-1}, \tag{2.3}$$

and the concentration of component j by

$$c^{(j)} \equiv \varrho^{(j)}/\varrho. \qquad (j = 1, \ldots, n) \tag{2.4}$$

From the preceding equation and (2.2) we have

$$\Sigma_{j=1}^{n} c^{(j)} = 1. \tag{2.5}$$

The barycentric velocity may be defined by

$$\mathbf{v} \equiv \Sigma_{j=1}^{n} c^{(j)} \mathbf{v}^{(j)}. \tag{2.6}$$

We now introduce a four-vector with components

$$m_\alpha \equiv \Sigma_{j=1}^{n} m_\alpha^{(j)}. \qquad (\alpha = 1, \ldots, 4) \tag{2.7}$$

It is easily seen that

$$m_1 = \varrho v_1;\ m_2 = \varrho v_2;\ m_3 = \varrho v_3;\ m_4 = ic\varrho. \tag{2.8}$$

We see that this four-vector represents the total flow of rest mass. By m we shall indicate the scalar

$$m \equiv (-\Sigma_{a=1}^{4} m_a^2)^{\frac{1}{2}} = \varrho(c^2 - \mathbf{v}^2)^{\frac{1}{2}}. \tag{2.9}$$

For the following considerations it is useful to introduce the dimensionless four-vector

$$u_a \equiv m_a/m. \qquad (a = 1, .., 4) \tag{2.10}$$

From this equation we have with (2.8) and (2.9)

$$\begin{aligned} u_1 &= v_1(c^2 - \mathbf{v}^2)^{-\frac{1}{2}};\ u_2 = v_2(c^2 - \mathbf{v}^2)^{-\frac{1}{2}}; \\ u_3 &= v_3(c^2 - \mathbf{v}^2)^{-\frac{1}{2}};\ u_4 = ic(c^2 - \mathbf{v}^2)^{-\frac{1}{2}}. \end{aligned} \tag{2.11}$$

We see that this four-vector can be interpreted as the four-dimensional analog of the barycentric velocity $\mathbf{v}$. Further, we see from the preceding equation that

$$\Sigma_{a=1}^{4} u_a^2 = -1, \tag{2.12}$$

hence, it follows that

$$\Sigma_{a=1}^{4} u_a(\partial u_a/\partial x_\beta) = 0. \qquad (\beta = 1, .., 4) \tag{2.13}$$

At any particular time we can assign to every point of the system a Lorentz frame in which $\mathbf{v}$ vanishes. We shall call this frame the barycentric Lorentz frame belonging to the point in the space-time continuum under consideration. *All quantities at a point in space-time continuum measured in the barycentric Lorentz frame belonging to this point will be distinguished by primes.* According to (2.9) we have then

$$\varrho' = m/c = \varrho(1 - \mathbf{v}^2/c^2)^{\frac{1}{2}}. \tag{2.14}$$

From this equation and (2.3) we have

$$v' = c/m, \tag{2.15}$$

and from (2.11) we have

$$u_a' = i\delta(a; 4), \qquad (a = 1, .., 4) \tag{2.16}$$

where $\delta(a; \beta)$ is the Kronecker symbol. Further, we have according to (2.4)

$$c'^{(j)} = \varrho'^{(j)}/\varrho'. \qquad (j = 1, ..., n) \tag{2.17}$$

We can show that $c'^{(j)}$ may also be expressed as

$$c'^{(j)} = -m^{-1}\,\Sigma_{\beta=1}^{4} u_\beta m_\beta^{(j)}. \qquad (j = 1, ..., n) \tag{2.18}$$

This can be done in the following way. In the first place we remark that the right hand side of this equati on is a scalar. Hence, if we prove the validity of (2.18) in one Lorentz frame we may infer that the equation is valid in any Lorentz frame. Inserting (2.1), (2.9) and (2.11) we find with the help of (2.4)

$$c'^{(j)} = \frac{c^2 - \mathbf{v}^{(j)} \cdot \mathbf{v}}{c^2 - \mathbf{v}^2}\, c^{(j)}. \quad (j = 1, \ldots, n) \quad (2.19)$$

It is seen that this equation is identically fulfilled in the barycentric Lorentz frame. Thus, (2.18) is proved and therefore (2.19) too. Furthermore,

$$\Sigma_{j=1}^{n}\, c'^{(j)} = 1. \quad (2.20)$$

The most convenient way to represent by four-vectors the *relative flows of matter* of the components with respect to the barycentric motion is

$$I_a^{(j)} \equiv m_a^{(j)} - c'^{(j)} m_a. \quad (a = 1, \ldots, 4;\ j = 1, \ldots, n) \quad (2.21)$$

Substitution of (2.1), (2.8) and (2.19) in this equation gives with the help of (2.4)

$$I_1^{(j)} = \varrho^{(j)}\left(v_1^{(j)} - \frac{c^2 - \mathbf{v}^{(j)} \cdot \mathbf{v}}{c^2 - \mathbf{v}^2}\, v_1\right); \quad I_2^{(j)} = \varrho^{(j)}\left(v_2^{(j)} - \frac{c^2 - \mathbf{v}^{(j)} \cdot \mathbf{v}}{c^2 - \mathbf{v}^2}\, v_2\right);$$

$$I_3^{(j)} = \varrho^{(j)}\left(v_3^{(j)} - \frac{c^2 - \mathbf{v}^{(j)} \cdot \mathbf{v}}{c^2 - \mathbf{v}^2}\, v_3\right); \quad I_4^{(j)} = ic\varrho^{(j)}\left(1 - \frac{c^2 - \mathbf{v}^{(j)} \cdot \mathbf{v}}{c^2 - \mathbf{v}^2}\right).$$

$$(j = 1, \ldots, n) \quad (2.22)$$

These equations give the flows in terms of densities and velocities. The four-vectors $I_a^{(j)}$ have been defined by the preceding equations in such a way as to have two important properties. First it follows from (2.21) with the help of (2.7) and (2.20)

$$\Sigma_{j=1}^{n}\, I_a^{(j)} = 0, \qquad (a = 1, \ldots, 4). \quad (2.23)$$

which expresses that the sum of the relative flows of all components vanishes. Further, we deduce from (2.21) with the help of (2.10), (2.12) and (2.18)

$$\Sigma_{a=1}^{4}\, u_a\, I_a^{(j)} = 0. \qquad (j = 1, \ldots, n) \quad (2.24)$$

From the last equation we see that all the relative flows, $I_a^{(j)}$, are perpendicular to the four-vector u_a representing the barycentric velocity.

We shall define the substantial derivative with respect to time as the Lorentz invariant operator

$$D \equiv c\, \Sigma_{a=1}^{4}\, u_a\, (\partial/\partial x_a). \quad (2.25)$$

With the help of (2.16) we see that

$$D = \partial/\partial t', \tag{2.26}$$

where t' is the time measured by an observer in the barycentric Lorentz frame.

The density of rest mass, $\varrho_{(0)}^{(j)}$, of component j measured by an observer *moving with this component* will be given by

$$\varrho_{(0)}^{(j)} = \varrho^{(j)} (1 - \mathbf{v}^{(j)2}/c^2)^{\frac{1}{2}}. \qquad (j = 1, \ldots, n) \tag{2.27}$$

In principle the quantities $\varrho_{(0)}^{(j)}$ and $\varrho'^{(j)}$ are different; however, in practical cases their difference in value is very small.

Finally, we introduce the tensor

$$\Delta_{\alpha\beta} \equiv \delta_{\alpha\beta} + u_\alpha u_\beta, \quad (\alpha, \beta = 1, .., 4) \tag{2.28}$$

$\delta_{\alpha\beta}$ being the Kronecker tensor. We immediately see that

$$\Delta_{\alpha\beta} = \Delta_{\beta\alpha}, \qquad (\alpha, \beta = 1, .., 4) \tag{2.29}$$

and with the help of (2.12) we deduce that

$$\Sigma_{\alpha=1}^4 u_\alpha \Delta_{\alpha\beta} = \Sigma_{\alpha=1}^4 \Delta_{\beta\alpha} u_\alpha = 0. \quad (\beta = 1, .., 4) \tag{2.30}$$

Using (2.16) it follows from (2.28) that

$$\Delta'_{\alpha\beta} = \delta(\alpha; \beta) - \delta(\alpha; 4)\, \delta(\beta; 4), \quad (\alpha, \beta = 1, .., 4) \tag{2.31}$$

or

$$\Delta'_{\alpha\beta} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}. \tag{2.32}$$

The sum of the diagonal elements of a tensor is a scalar. Using (2.28) and (2.12) we get for the sum of the diagonal elements of $\Delta_{\alpha\beta}$

$$\Sigma_{\alpha=1}^4 \Delta_{\alpha\alpha} = 3. \tag{2.33}$$

In the following it is seen that the tensor $\Delta_{\alpha\beta}$ $(\alpha, \beta = 1, .., 4)$ plays the role which $\delta_{\alpha\beta}(\alpha, \beta = 1, 2, 3)$ has in the non-relativistic theory. From (2.10), (2.18), (2.21) and (2.28) we have

$$I_\alpha^{(j)} = \Sigma_{\beta=1}^4 \Delta_{\alpha\beta}\, m_\beta^{(j)}. \quad (\alpha = 1, .., 4;\ j = 1, \ldots, n) \tag{2.34}$$

§ 3. *The energy-momentum tensor and some deduced quantities.* In this section we shall consider the energy-momentum tensor and some other quantities which may be defined with its help. We denote by $e_{(v)}$ the energy per unit volume and by $\mathbf{J}_{(e)}$ the energy flow. In principle both quantities differ from the corresponding non-relativistic quantities because the theory of relativity recognizes the fact that mass is a form of energy. Since the barycentric Lorentz frame is defined in such a way that the total mass flow vanishes, $\mathbf{J}'_{(e)}$ corresponds closely to the non-relativistic energy flow in the barycentric Lorentz frame. According to the theory of relativity an energy flow is associated with a momentum density $\mathbf{g}$ given by

$$\mathbf{g} = c^{-2}\,\mathbf{J}_{(e)}. \tag{3.1}$$

We write the energy-momentum tensor in the form

$$W_{\alpha\beta} = t_{\alpha\beta} + g_\alpha v_\beta \;\; (\alpha, \beta = 1, 2, 3); \qquad W_{\alpha 4} = icg_\alpha \;\; (\alpha = 1, 2, 3);$$
$$W_{4\alpha} = ic^{-1} J_{(e)\alpha} \quad (\alpha = 1, 2, 3); \;\; W_{44} = -\, e_{(v)}. \tag{3.2}$$

The $W_{\alpha\beta}$ ($\alpha, \beta = 1, 2, 3$) correspond to the momentum flows. These terms have been split up into a part $g_\alpha v_\beta$ corresponding to the transfer of momentum with the barycentric velocity (convective part) and a remaining part which defines the stress tensor. According to (3.1) we have $W_{\alpha 4} = W_{4\alpha}$ ($\alpha = 1, 2, 3$) and we extend this by assuming $W_{\alpha\beta}$ to be a symmetric tensor. Thus,

$$W_{\alpha\beta} = W_{\beta\alpha}. \qquad (\alpha, \beta = 1, \ldots, 4) \tag{3.3}$$

This symmetry is a well-known and general feature of the energy-momentum tensor.

It is easily shown that $e'_{(v)}$ is given by

$$e'_{(v)} = \Sigma^4_{\gamma,\zeta=1}\, u_\gamma\, W_{\gamma\zeta}\, u_\zeta. \tag{3.4}$$

The right hand side of this equation is Lorentz invariant. If we calculate the right hand side in the barycentric Lorentz frame we get with (2.16) and (3.2) just the left hand side. Hence, the equation is proved.

We represent the heat flow by a four-vector defined by

$$I^{(0)}_\alpha \equiv -\, c\, \Sigma^4_{\gamma,\zeta=1}\, \Delta_{\alpha\gamma} W_{\gamma\zeta}\, u_\zeta. \qquad (\alpha = 1, \ldots, 4) \tag{3.5}$$

With the help of (2.16), (2.31), (3.2) and (3.3) we find from the preceding definition

$$I'^{(0)}_1 = J'_{(e)1}; \quad I'^{(0)}_2 = J'_{(e)2}; \quad I'^{(0)}_3 = J'_{(e)3}; \quad I'^{(0)}_4 = 0. \tag{3.6}$$

From this equation we see that $I'^{(0)}_\alpha$ corresponds to $\mathbf{J}'_{(e)}$. Further, $\mathbf{J}'_{(e)}$ corresponds to the non-relativistic energy flow in the barycentric Lorentz frame as was stressed above. The heat flow in the non-relativistic thermodynamics of irreversible processes is usually defined in such a way that it equals the energy flow in the barycentric frame. (Discussion of various ways to define the heat flow in ref. 4). From these considerations it follows that $I_\alpha^{(0)}$ may represent the heat flow. With the help of (3.5) and (2.30) the following important property of the heat flow may be derived

$$\Sigma_{\alpha=1}^{4} u_\alpha I_\alpha^{(0)} = 0, \tag{3.7}$$

showing that $I_\alpha^{(0)}$ is perpendicular to the four-vector u_α representing the barycentric velocity (cf. (2.24)).

Further, we may represent the stresses by the tensor

$$w_{\alpha\beta} \equiv \Sigma_{\gamma,\zeta=1}^{4} \Delta_{\alpha\gamma} W_{\gamma\zeta} \Delta_{\zeta\beta}. \quad (\alpha, \beta = 1, \ldots, 4) \tag{3.8}$$

As a matter of fact we find from this definition with the help of (2.31) and (3.2)

$$w'_{\alpha\beta} = t'_{\alpha\beta} \ (\alpha, \beta = 1, 2, 3); \quad w'_{\alpha 4} = w'_{4\alpha} = 0 \quad (\alpha = 1, \ldots, 4), \tag{3.9}$$

showing that $w_{\alpha\beta}$ indeed may represent the stresses. From (2.29), (3.3) and (3.8) it follows that

$$w_{\alpha\beta} = w_{\beta\alpha}, \qquad (\alpha, \beta = 1, \ldots, 4) \tag{3.10}$$

and from (3.8) and (2.30) we have

$$\Sigma_{\alpha=1}^{4} u_\alpha w_{\alpha\beta} = \Sigma_{\alpha=1}^{4} w_{\beta\alpha} u_\alpha = 0. \qquad (\beta = 1, \ldots, 4) \tag{3.11}$$

The equations (3.10) and (3.11) reduce the number of independent components of the tensor $w_{\alpha\beta}$ to six.

It may be readily verified that

$$W_{\alpha\beta} = u_\alpha u_\beta e'_{(v)} + c^{-1}(u_\beta I_\alpha^{(0)} + u_\alpha I_\beta^{(0)}) + w_{\alpha\beta} \quad (\alpha, \beta = 1, \ldots, 4) \tag{3.12}$$

by substituting (3.4), (3.5) and (3.8) in the right hand side of this equation and making use of (2.28) and (3.3).

We now define, analogous to the specific internal energy in non-relativistic thermodynamics, the specific energy measured by an observer in the barycentric Lorentz frame by

$$e' \equiv v' e'_{(v)} - a, \tag{3.13}$$

where a is an arbitrary constant, fixing the zero point of e'. It will appear that a drops out of the final results.

By p' we denote the hydrostatic pressure measured in the barycentric Lorentz frame. We may define as viscous stress tensor

$$P_{\alpha\beta} \equiv - w_{\alpha\beta} + p' \Delta_{\alpha\beta}. \quad (\alpha, \beta = 1, \ldots, 4) \tag{3.14}$$

From the preceding definition we have with the help of (2.32) and (3.9)

$$P'_{\alpha\beta} = -t'_{\alpha\beta} + p'\delta_{\alpha\beta} \quad (\alpha, \beta = 1, 2, 3); \quad P'_{\alpha 4} = P'_{4\alpha} = 0 \quad (\alpha = 1, \ldots, 4), \quad (3.15)$$

showing that $P_{\alpha\beta}$ indeed may represent the viscous stress tensor. From (2.29) and (3.10) it follows

$$P_{\alpha\beta} = P_{\beta\alpha}, \qquad (\alpha, \beta = 1, \ldots, 4) \quad (3.16)$$

and from (2.30) and (3.11) we have

$$\Sigma_{\alpha=1}^{4}\, u_\alpha P_{\alpha\beta} = \Sigma_{\alpha=1}^{4}\, P_{\beta\alpha} u_\alpha = 0. \quad (\beta = 1, \ldots, 4) \quad (3.17)$$

We shall not introduce the simplifying assumption $p' = \frac{1}{3}\, \Sigma_{\alpha=1}^{4}\, w_{\alpha\alpha}$ so that volume viscosity effects will not be neglected.

§ 4. *The fundamental laws.* We can now formulate four fundamental laws which are the starting point for the calculation of the entropy production.

I. The balance equation for rest mass. We assume one chemical reaction among the components of the system. We shall denote by $\nu^{(k)} J_{(c)}$ the chemical production of rest mass of component k per unit volume and per unit time. It is obvious that this quantity is Lorentz invariant. The quantity $\nu^{(k)}$ divided by the molecular mass of substance k is proportional to the stoechiometric number of this component in the chemical reaction. Thus, $\nu^{(k)}$ is Lorentz invariant too. Hence, it follows that $J_{(c)}$, called the chemical reaction rate in mass per unit volume and per unit time, is also Lorentz invariant. Now, we can write the balance equation for rest mass in the form

$$\partial \varrho^{(k)} / \partial t = -\operatorname{div} \varrho^{(k)} \mathbf{v}^{(k)} + \nu^{(k)} J_{(c)}. \qquad (k = 1, \ldots, n) \quad (4.1)$$

(For several reactions the last term would be a sum of similar expressions for each reaction). With the help of (2.1) we can write this law in four-dimensional form,

$$\Sigma_{\alpha=1}^{4}\, \partial m_\alpha^{(k)} / \partial x_\alpha = \nu^{(k)} J_{(c)}. \quad (k = 1, \ldots, n) \quad (4.2)$$

Hence, it follows that this law is Lorentz invariant. Summing the n equations (4.2) over all values of k, we get with the help of (2.7) and of $\Sigma_{k=1}^{n}\, \nu^{(k)} = 0$

$$\Sigma_{\alpha=1}^{4}\, \partial m_\alpha / \partial x_\alpha = 0. \quad (4.3)$$

This means that total rest mass is conserved.

II. The momentum and energy law. We shall assume that external forces working on the system only depend on space and time coordinates. If $\mathbf{F}^{(k)}$ is the force per unit mass on component k, we can define, as is well-known, a four-vector with components

$$K_1^{(k)} \equiv \varrho^{(k)} F_1^{(k)} / \varrho_{(0)}^{(k)};\ K_2^{(k)} \equiv \varrho^{(k)} F_2^{(k)} / \varrho_{(0)}^{(k)};\ K_3^{(k)} \equiv \varrho^{(k)} F_3^{(k)} / \varrho_{(0)}^{(k)};$$
$$K_4^{(k)} \equiv i\varrho^{(k)} (\mathbf{v}^{(k)} \cdot \mathbf{F}^{(k)})/(c\varrho_{(0)}^{(k)}).\quad (k = 1, \ldots, n) \quad (4.4)$$

From (2.1) and the preceding equation we have

$$\Sigma_{\alpha=1}^{4}\, m_\alpha^{(j)} K_\alpha^{(j)} = 0. \qquad (j = 1, \ldots, n) \qquad (4.5)$$

Thus, we see that the vectors $m_\alpha^{(j)}$ and $K_\alpha^{(j)}$ are perpendicular. The balance equation for momentum is expressed by

$$\partial g_\alpha/\partial t + \Sigma_{\beta=1}^{3}\, \partial(g_\alpha v_\beta)/\partial x_\beta = \Sigma_{j=1}^{n}\, \varrho^{(j)} F_\alpha^{(j)} - \Sigma_{\beta=1}^{3}\, \partial t_{\alpha\beta}/\partial x_\beta. \quad (\alpha = 1,2,3)\ (4.6)$$

The energy balance reads

$$\partial e_{(v)}/\partial t = -\operatorname{div} \mathbf{J}_{(e)} + \Sigma_{j=1}^{n}\, \varrho^{(j)}\, \mathbf{v}^{(j)} \cdot \mathbf{F}^{(j)}. \qquad (4.7)$$

With the help of (3.2) and (4.4) we can combine (4.6) and (4.7) into the four-dimensional equation

$$\Sigma_{\beta=1}^{4}\, \partial W_{\alpha\beta}/\partial x_\beta = \Sigma_{j=1}^{n}\, \varrho_{(0)}^{(j)} K_\alpha^{(j)}, \quad (\alpha = 1, \ldots, 4) \qquad (4.8)$$

showing the relativistic invariance of the two laws.

III. The second law of thermodynamics (Gibbs relation). Just as in the non-relativistic thermodynamics of irreversible processes we assume that the second law,

$$T'(\partial s'/\partial t') = \partial e'/\partial t' + p'(\partial v'/\partial t') - \Sigma_{j=1}^{n}\, \mu'^{(j)}(\partial c'^{(j)}/\partial t'), \qquad (4.9)$$

is valid in the barycentric frame. T is the temperature, s the specfic entropy and $\mu^{(j)}$ the partial specific Gibbs function of component j (chemical potential). With the help of the Lorentz invariant operator D defined by (2.25) we can write

$$T'Ds' = De' + p'Dv' - \Sigma_{j=1}^{n}\, \mu'^{(j)} Dc'^{(j)}. \qquad (4.10)$$

The quantities with primes, measured in the barycentric frame, are here expressed as functions of space coordinates and time in an arbitrary Lorentz frame.

§ 5. *The first law of thermodynamics.* In the non-relativistic theory the first law of thermodynamics is obtained by multiplying the momentum law by $\mathbf{v}$ and subtracting the result from the energy equation. By multiplying the equation (4.8) by u_α and summing the result over all values of α, it is obvious that we perform an analogous procedure. Therefore, we must study the equation

$$\Sigma_{\alpha,\beta=1}^{4} u_\alpha(\partial W_{\alpha\beta}/\partial x_\beta) = \Sigma_{j=1}^{n} \Sigma_{\alpha=1}^{4} \varrho_{(0)}^{(j)} u_\alpha K_\alpha^{(j)} \tag{5.1}$$

in more detail.

With the help of (2.10), (2.21) and (4.5) we can transform the right hand side of this equation into

$$\Sigma_{j=1}^{n} \Sigma_{\alpha=1}^{4} \varrho_{(0)}^{(j)} u_\alpha K_\alpha^{(j)} = \Sigma_{j=1}^{n} \Sigma_{\alpha=1}^{4} \varrho_{(0)}^{(j)} (mc'^{(j)})^{-1} c'^{(j)} m_\alpha K_\alpha^{(j)} = \\ = - \Sigma_{j=1}^{n} \Sigma_{\alpha=1}^{4} c^{-1} \omega^{(j)} I_\alpha^{(j)} K_\alpha^{(j)}, \tag{5.2}$$

with the Lorentz invariant quantity $\omega^{(j)}$ being defined by

$$\omega^{(j)} \equiv \varrho_{(0)}^{(j)} c(mc'^{(j)})^{-1}. \qquad (j = 1, \ldots, n) \tag{5.3}$$

Considering the left hand side of (5.1) we have, with the help of (3.12)

$$\Sigma_{\alpha,\beta=1}^{4} u_\alpha(\partial W_{\alpha\beta}/\partial x_\beta) = \\ = \Sigma_{\beta=1}^{4} (\partial/\partial x_\beta) [\Sigma_{\alpha=1}^{4} u_\alpha \{u_\alpha u_\beta e'_{(v)} + c^{-1} (u_\beta I_\alpha^{(0)} + u_\alpha I_\beta^{(0)}) + w_{\alpha\beta}\}] - \\ - \Sigma_{\alpha,\beta=1}^{4} \{u_\alpha u_\beta e'_{(v)} + c^{-1}(u_\beta I_\alpha^{(0)} + u_\alpha I_\beta^{(0)}) + w_{\alpha\beta}\} (\partial u_\alpha/\partial x_\beta). \tag{5.4}$$

Using the relations (2.12), (2.13), (3.7) and (3.11) we may simplify this expression

$$\Sigma_{\alpha,\beta=1}^{4} u_\alpha(\partial W_{\alpha\beta}/\partial x_\beta) = \\ = -\Sigma_{\beta=1}^{4} (\partial/\partial x_\beta) (u_\beta e'_{(v)} + c^{-1} I_\beta^{(0)}) - \Sigma_{\alpha,\beta=1}^{4} (c^{-1} u_\beta I_\alpha^{(0)} + w_{\alpha\beta}) (\partial u_\alpha/\partial x_\beta). \tag{5.5}$$

Now we transform two terms on the right hand side of (5.5). With the help of (2.10), (2.14), (2.15), (2.25), (3.13) and (4.3) we deduce

$$\Sigma_{\beta=1}^{4} (\partial/\partial x_\beta) (u_\beta e'_{(v)}) = c^{-1} \varrho' De'. \tag{5.6}$$

With (2.10), (2.13), (2.14), (2.15), (2.25), (2.28) and (4.3) we deduce

$$\Sigma_{\alpha,\beta=1}^{4} \Delta_{\alpha\beta}(\partial u_\beta/\partial x_\alpha) = c^{-1} \varrho' Dv', \tag{5.7}$$

and from this equation and (3.14) we have

$$\Sigma_{\alpha,\beta=1}^{4} w_{\alpha\beta}(\partial u_\beta/\partial x_\alpha) = c^{-1} \varrho' p' Dv' - \Sigma_{\alpha,\beta=1}^{4} P_{\alpha\beta}(\partial u_\beta/\partial x_\alpha). \tag{5.8}$$

Substitution of (5.6) and (5.8) into (5.5) and the use of the definition (2.25) gives

$$\Sigma_{\alpha,\beta=1}^{4} u_\alpha(\partial W_{\alpha\beta}/\partial x_\beta) = - c^{-1} \varrho' De' - c^{-1} \Sigma_{\beta=1}^{4} (\partial I_\beta^{(0)}/\partial x_\beta + c^{-1} I_\beta^{(0)} Du_\beta) - \\ - c^{-1} \varrho' p' Dv' + \Sigma_{\alpha,\beta=1}^{4} P_{\alpha\beta}(\partial u_\beta/\partial x_\alpha). \tag{5.9}$$

Substitution of the results (5.9) and (5.2) into (5.1) gives the equation

$$\varrho'(De' + p'Dv') = - \Sigma_{\beta=1}^{4} (\partial I_{\beta}^{(0)}/\partial x_{\beta} + c^{-1} I_{\beta}^{(0)} Du_{\beta}) + \\ + \Sigma_{j=1}^{n} \Sigma_{\alpha=1}^{4} \omega^{(j)} I_{\alpha}^{(j)} K_{\alpha}^{(j)} + c\, \Sigma_{\alpha,\beta=1}^{4} P_{\alpha\beta} (\partial u_{\beta}/\partial x_{\alpha}), \quad (5.10)$$

which may be considered as the first law of thermodynamics for the energy e'. The left hand side of this equation is completely analogous to the left hand side of the corresponding equation of the non-relativistic theory. The first term on the right hand side of (5.10) corresponds to the divergence of the heat flow in the non-relativistic theory. It should be remarked, however, that in (5.10) the four-dimensional divergence of the heat flow occurs. The second term on the right hand side has no non-relativistic analog and was first found by Eckart. The third and fourth terms are analogous to the corresponding non-relativistic ones, viz. energy dissipated by external forces and by viscous stresses.

§ 6. *The entropy balance.* In the preceding section we derived the first law of thermodynamics from the balance equation for the energy with the help of the momentum and mass laws. We shall now calculate the entropy balance from the first and second laws of thermodynamics and the balance equation for rest mass.

We first derive with the aid of (2.10), (2.14), (2.21), (2.25), (4.2) and (4.3)

$$Dc'^{(j)} = (1/\varrho') \Sigma_{\alpha=1}^{4} (\partial/\partial x_{\alpha}) (c'^{(j)} m_{\alpha}) = -(1/\varrho') \{\Sigma_{\alpha=1}^{4} (\partial I_{\alpha}^{(j)}/\partial x_{\alpha}) - \nu^{(j)} J^{(c)}\}. \\ (j = 1, \ldots, n) \quad (6.1)$$

Substitution of this expression and (5.10) into (4.10) gives after some calculation

$$\varrho' Ds' = - \Sigma_{\alpha=1}^{4} (\partial/\partial x_{\alpha}) \{(1/T') (I_{\alpha}^{(0)} - \Sigma_{j=1}^{n} \mu'^{(j)} I_{\alpha}^{(j)})\} - \\ - (1/T') \Sigma_{\alpha=1}^{4} I_{\alpha}^{(0)} \{(1/T') (\partial T'/\partial x_{\alpha}) + c^{-1} Du_{\alpha}\} + \\ + (1/T') [\Sigma_{j=1}^{n} \Sigma_{\alpha=1}^{4} I_{\alpha}^{(j)} \{\omega^{(j)} K_{\alpha}^{(j)} - T' (\partial/\partial x_{\alpha}) (\mu'^{(j)}/T')\} + \\ + c\, \Sigma_{\alpha,\beta=1}^{4} P_{\alpha\beta} (\partial u_{\beta}/\partial x_{\alpha})] - (1/T') J_{(c)} \Sigma_{j=1}^{n} \nu^{(j)} \mu'^{(j)}. \quad (6.2)$$

We now define the scalar quantity

$$\Pi \equiv \tfrac{1}{3} \Sigma_{\alpha=1}^{4} P_{\alpha\alpha}. \quad (6.3)$$

Substitution of (3.14) into the preceding equation gives with the help of (2.33)

$$\Pi = p' - \tfrac{1}{3} \Sigma_{\alpha=1}^{4} w_{\alpha\alpha}. \quad (6.4)$$

From this equation we see that Π is the difference between the hydrostatic pressure and $\frac{1}{3}$ of the sum of the diagonal elements of the stress tensor. Further, we introduce the tensor

$$\bar{P}_{\alpha\beta} \equiv P_{\alpha\beta} - \Pi \Delta_{\alpha\beta}. \quad (\alpha, \beta = 1, \ldots, 4) \quad (6.5)$$

Using (6.3) and (2.33) we have from the preceding equation

$$\Sigma_{\alpha=1}^{4} \bar{P}_{\alpha\alpha} = 0. \quad (6.6)$$

With the aid of (2.29) and (3.16) we immediately see from (6.5) that

$$\bar{P}_{\alpha\beta} = \bar{P}_{\beta\alpha}, \quad (\alpha, \beta = 1, \ldots, 4) \quad (6.7)$$

and from (2.30) and (3.17) we have

$$\Sigma_{\alpha=1}^{4} u_\alpha \bar{P}_{\alpha\beta} = \Sigma_{\alpha=1}^{4} \bar{P}_{\beta\alpha} u_\alpha = 0. \quad (\beta = 1, \ldots, 4) \quad (6.8)$$

We now define as "forces" ("affinities") the four-vectors

$$Y_\alpha^{(0)} \equiv -\{(1/T')(\partial T'/\partial x_\alpha) + c^{-1} Du_\alpha\}, \quad (\alpha = 1, \ldots, 4) \quad (6.9)$$

$$Y_\alpha^{(j)} \equiv \omega^{(j)} K_\alpha^{(j)} - T'(\partial/\partial x_\alpha)(\mu'^{(j)}/T'), \quad (\alpha = 1, \ldots, 4; j = 1, \ldots, n) \quad (6.10)$$

and the scalar

$$A = -\Sigma_{j=1}^{n} \nu^{(j)} \mu'^{(j)}. \quad (6.11)$$

Substituting (6.5) and the three preceding equations into (6.2) gives with the aid of (5.7)

$$\varrho' Ds' = -\Sigma_{\alpha=1}^{4} (\partial/\partial x_\alpha)\{(1/T')(I_\alpha^{(0)} - \Sigma_{j=1}^{n} \mu'^{(j)} I_\alpha^{(j)})\} +$$
$$+ (1/T')[\Sigma_{j=0}^{n} \Sigma_{\alpha=1}^{4} I_\alpha^{(j)} Y_\alpha^{(j)} + c\,\Sigma_{\alpha,\beta=1}^{4} \bar{P}_{\alpha\beta}(\partial u_\beta/\partial x_\alpha) + \Pi \varrho' Dv' + J_{(c)} A]. \quad (6.12)$$

The first and second parts on the right-hand side of this expression are analogous respectively to the divergence of the entropy flow and the entropy production of the non-relativistic theory. The first term in the second part contains the contribution of the heat conduction ($j = 0$) and the diffusion ($j \neq 0$), the second and third terms the contributions of ordinary and volume viscosity, and the last term the contribution of the chemical reaction.

§ 7. *The phenomenological equations and the Onsager relations.* Taking into account Curie's law we introduce the phenomenological laws in such a way that a certain flux only depends on forces having the same tensorial character as this flux. On the other hand, this flux may depend on all the forces having its tensorial character.

Therefore, we introduce for the vectorial fluxes and forces $I_\alpha^{(j)}$ and $Y_\alpha^{(j)}$ the equations

$$I_\alpha^{(j)} = \Sigma_{k=0}^{n} \Sigma_{\beta=1}^{4} L_{\alpha\beta}^{(j)(k)} Y_\beta^{(k)}, \quad (\alpha = 1, \ldots, 4; j = 0, 1, \ldots, n) \quad (7.1)$$

where the $L^{(j)(k)}_{\alpha\beta}$ are $(n+1)^2$ tensors $(j, k = 0, 1, \ldots, n)$ each having 4^2 components $(\alpha, \beta = 1, \ldots, 4)$.

We shall now show that we can derive an explicit form for $L^{(j)(k)}_{\alpha\beta}$ from the assumption that the medium is isotropic, using the postulate that all equations should correspond closely to the non-relativistic equations in the barycentric Lorentz frame. From (2.22) we have

$$I'^{(j)}_{\alpha} = \varrho'^{(j)} v'^{(j)}_{\alpha} \quad (\alpha = 1, 2, 3;\ j = 1, \ldots, n);$$
$$I'^{(j)}_{4} = 0 \qquad (j = 1, \ldots, n). \tag{7.2}$$

Using (2.14) and (2.17) we have from (5.3)

$$\omega^{(j)} = \varrho^{(j)}_{(0)}/\varrho'^{(j)}. \qquad (j = 1, \ldots, n) \tag{7.3}$$

Substitution of the preceding equation and (4.4) in (6.10) gives

$$Y'^{(j)}_{\alpha} = F'^{(j)}_{\alpha} - T'(\partial/\partial x'_{\alpha})\,(\mu'^{(j)}/T') \qquad (\alpha = 1, 2, 3;\ j = 1, \ldots, n);$$
$$Y'^{(j)}_{4} = (i/c)\,\mathbf{v}'^{(j)} \cdot \mathbf{F}'^{(j)} + (iT'/c)\,(\partial/\partial t')\,(\mu'^{(j)}/T') \quad (j = 1, \ldots, n). \tag{7.4}$$

From (7.2) and (7.4) and from (3.6) and (6.9) we may conclude that (7.1) corresponds to the non-relativistic equations for an isotropic medium in the barycentric Lorentz frame if

$$L'^{(j)(k)}_{\alpha\beta} = L^{(j)(k)}\,\{\delta(\alpha;\beta) - \delta(\alpha;4)\,\delta(\beta;4)\},$$
$$(\alpha, \beta = 1, \ldots, 4;\ j, k = 0, 1, \ldots, n) \tag{7.5}$$

where the $L^{(j)(k)}$ are the phenomenological coefficients from the non-relativistic theory. With the help of (2.31) we may write for (7.5)

$$L'^{(j)(k)}_{\alpha\beta} = L^{(j)(k)}\,\Delta'_{\alpha\beta}. \quad (\alpha, \beta = 1, \ldots, 4;\ j, k = 0, 1, \ldots, n) \tag{7.6}$$

Since if two tensors are equal in one Lorentz frame they are equal in all Lorentz frames, we may conclude from (7.6)

$$L^{(j)(k)}_{\alpha\beta} = L^{(j)(k)}\,\Delta_{\alpha\beta}. \quad (\alpha, \beta = 1, \ldots, 4;\ j, k = 0, 1, \ldots, n) \tag{7.7}$$

As the $L^{(j)(k)}$ are the phenomenological coefficients from the non-relativistic theory we have among them the Onsager relations

$$L^{(j)(k)} = L^{(k)(j)}. \qquad (j, k = 0, 1, \ldots, n) \tag{7.8}$$

From (2.29) and the two preceding equations we get

$$L^{(j)(k)}_{\alpha\beta} = L^{(k)(j)}_{\alpha\beta} = L^{(j)(k)}_{\beta\alpha} = L^{(k)(j)}_{\beta\alpha}. \quad (\alpha, \beta = 1, \ldots, 4;\ j, k = 0, 1, \ldots, n) \tag{7.9}$$

We see that the Onsager relations enter again in the relativistic theory, and that they are invariant under Lorentz transformations.

In a mixture with n chemical components we may have $n - 1$ independent relative flows of matter and one heat flow. Together these flows have $3n$ components in ordinary space. Hence, we should expect $3n$ independent phenomenological equations; however, (7.1) gives $4(n + 1)$ equations. Therefore, we must now prove that $n + 4$ of the equations are dependent on the others. From (2.30) and (7.7) follows

$$\Sigma_{\alpha=1}^{4} u_\alpha \left(\Sigma_{\beta=1}^{4} \Sigma_{k=0}^{n} L_{\alpha\beta}^{(j)(k)} Y_\beta^{(k)}\right) = 0. \qquad (j = 0, 1, \ldots, n) \qquad (7.10)$$

According to (2.11) we have $u_4 \neq 0$ in every Lorentz frame. Hence, from the preceding equation, (2.24) and (3.7) we may draw the conclusion that in (7.1) for each value of j the equation with $\alpha = 4$ depends on the equations with $\alpha = 1, 2, 3$ for the same value of j. This reduces the number of independent equations by $n + 1$. As is well known from the non-relativistic theory we have

$$\Sigma_{j=1}^{n} L^{(j)(k)} = 0. \qquad (k = 0, 1, \ldots, n) \qquad (7.11)$$

Using the preceding equation and (7.7) we find

$$\Sigma_{j=1}^{n} \left(\Sigma_{\beta=1}^{4} \Sigma_{k=0}^{n} L_{\alpha\beta}^{(j)(k)} Y_\beta^{(k)}\right) = 0. \; (\alpha = 1, 2, 3) \qquad (7.12)$$

From this equation and (2.23) we see that in (7.1) for $\alpha = 1, 2$ or 3 the equation with $j = n$ depends on the equations with $j = 1, 2, \ldots, n - 1$ for the same value of α, and this reduces the number of independent equations by 3. Thus, finally, we get the right number of $3n$ independent equations.

It should be emphasized that the term $c^{-1} Du_\alpha$, occurring in (6.9) represents an effect which the non-relativistic theory does not predict. This term, discovered already by Eckart [1]), shows that acceleration of matter causes a heat flow. Moreover, as we now see, it also gives a cross-effect with diffusion.

For the tensor $\bar{P}_{\alpha\beta}$ we may introduce the phenomenological equations

$$\bar{P}_{\alpha\beta} = c \, \Sigma_{\gamma,\zeta=1}^{4} L_{\alpha\beta\gamma\zeta} \, (\partial u_\gamma / \partial x_\zeta), \qquad (\alpha, \beta = 1, \ldots, 4) \qquad (7.13)$$

where $L_{\alpha\beta\gamma\zeta}$ is a tensor of the fourth order. Taking into account the assumption that the medium is isotropic, the postulate that all equations have to correspond closely to the equations of the non-relativistic theory in the barycentric frame, and the equation (6.6) which expresses that the sum of the diagonal elements of $\bar{P}_{\alpha\beta}$

vanishes, we may derive, along the same lines which gave the result (7.7), a form for $L_{\alpha\beta\gamma\zeta}$ which leads to the equation

$$\bar{P}_{\alpha\beta} = \eta c \Sigma^4_{\gamma,\zeta=1} [\Delta_{\alpha\gamma}\Delta_{\beta\zeta}\{(\partial u_\gamma/\partial x_\zeta) + (\partial u_\zeta/\partial x_\gamma)\} - \tfrac{2}{3}\Delta_{\alpha\beta}\Delta_{\gamma\zeta}(\partial u_\gamma/\partial x_\zeta)], \quad (\alpha, \beta = 1, .., 4) \quad (7.14)$$

where the scalar η is the ordinary viscosity. Again, we may show that among the sixteen equations given by (7.14) seven equations are dependent on the others. This reduces the number of independent equations to nine, which would be expected from physical considerations.

For the scalar quantities Π and $J_{(c)}$ we may introduce phenomenological equations of the form

$$\Pi = \eta_{(v)}\varrho' Dv' + L_{(p)(c)} A, \quad (7.15)$$

$$J_{(c)} = L_{(c)(p)} \varrho' Dv' + LA, \quad (7.16)$$

where $\eta_{(v)}$ is called the volume viscosity. All quantities occurring in (7.15) and (7.16) are Lorentz invariant. The Onsager relations, in the Casimir form, read

$$L_{(c)(p)} = -L_{(p)(c)}. \quad (7.17)$$

Substitution of (7.14) and (7.15) in (6.5) gives

$$P_{\alpha\beta} = \eta c \Sigma^4_{\gamma,\zeta=1} [\Delta_{\alpha\gamma}\Delta_{\beta\zeta}\{(\partial u_\gamma/\partial x_\zeta) + (\partial u_\zeta/\partial x_\gamma)\} - \tfrac{2}{3}\Delta_{\alpha\beta}\Delta_{\gamma\zeta}(\partial u_\gamma/\partial x_\zeta)] + \\ + \eta_{(v)} \Delta_{\alpha\beta} \varrho' Dv' + L_{(p)(c)} \Delta_{\alpha\beta} A. \quad (\alpha, \beta = 1, .., 4) \quad (7.18)$$

The first term in (7.16) and the last terms in (7.15) and (7.18) represent cross-effects of volume viscosity and chemical reactions which one could call "visco-chemical" effects.

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