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ON THE THERMODYNAMICS OF IRREVERSIBLE HEAT AND MASS TRANSFER

S. R. DE GROOT
Lorentz-Institute, University of Leyden, Leyden, the Netherlands

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Abstract—"Non-equilibrium thermodynamics" can serve as a basis for a macroscopic treatment of the irreversible phenomena. It is shown for a system in which heat conduction, diffusion, viscous flow, etc. can take place, how one can find a complete set of differential equations, describing the irreversible behaviour, from the relevant conservation laws, entropy balance and phenomenological equations.

1. INTRODUCTION

THE entropy of a system can change in two ways: either by external supply of heat or matter, or by production of entropy inside the system. The first change may be positive, zero or negative, depending on the interaction of the system with its surroundings. The second change, the entropy production, which arises from irreversible processes taking place inside the system, is positive according to the second law of thermodynamics. In classical thermodynamics one is usually satisfied with this statement in the form of an inequality. In the so-called "thermodynamics of irreversible processes" or "non-equilibrium thermodynamics" however, one wishes to derive an expression for the magnitude of the entropy production which characterizes the irreversibility of the phenomena.

The procedure followed in non-equilibrium thermodynamics consists of first establishing the various conservation laws of macroscopic physics: the laws of conservation of matter, momentum, angular momentum and energy. (In section 2 of this paper we give the forms which these laws take for an isotropic fluid in which heat conduction, diffusion of matter and viscous flow can occur. In sections 4 and 5 we study the effects caused by chemical reactions, relaxation processes and external forces.) Then Gibbs' entropy law is written and an entropy balance equation is established with the help of the conservation laws. This balance equation contains as a source term the entropy production strength. The expression for the entropy production found in this way consists of a sum of contributions arising from heat conduction, diffusion, viscous flow and chemical reactions (sections 3, 4 and 5). Each of these contributions consists of a product of a flux (such as the heat flow or the diffusion flow) and a "thermodynamic force" (such as the temperature gradient or the concentration gradient). One can establish linear relationships (called phenomenological equations) between these fluxes and thermodynamic forces (section 6). The coefficients occurring in these equations are heat conductivities, diffusion coefficients and the like. Certain relations exist between these coefficients as a result of time reversal invariance (the Onsager relations) and of possible spatial symmetries of the system (the Curie principle). Finally one obtains a complete set of differential equations describing the system by inserting the phenomenological equations into the conservation and entropy laws and by writing down the appropriate equations of state (section 7).

A variety of irreversible phenomena have been studied by the method outlined above [1–3], e.g., besides the processes mentioned already, thermal diffusion, thermo-electricity, heat conduction in reacting mixtures, electric conduction, electric and magnetic relaxation, sound dispersion and absorption, etc.

Two points of special interest must still be mentioned. In the first place the use of thermodynamical concepts, such as entropy, outside equilibrium needs justification and the Onsager relations must be proved. Both these problems can be discussed on the basis of statistical mechanics, e.g., the theory of stochastic processes or the kinetic theory of matter [3].

The second point of interest is the practical application of the theory. To this end the differential equations referred to above must be solved by using the necessary initial and boundary conditions. Progress has been made in obtaining analytical and numerical results of technical importance these last years [4].

2. THE CONSERVATION LAWS

We shall establish the basic conservation laws of mass, momentum, angular momentum and energy in a way which is appropriate for non-uniform systems: in the so-called "local" form, i.e. with physical quantities as field variables which are continuous functions of the space co-ordinates and of time.

(a) *Conservation of mass* is expressed by

$$\frac{\partial \rho_k}{\partial t} = -\mathrm{div}\, \rho_k \mathbf{v}_k, \quad (k = 1, 2, \ldots, n), \quad (1)$$

where ρ_k is the density of component k of a mixture of n non-reacting components, and $\mathbf{v}_k$ its velocity (both continuous functions of space variables and of time). An alternative form of (1) is

$$\rho \frac{\mathrm{d}c_k}{\mathrm{d}t} = -\mathrm{div}\, \mathbf{J}_k, \quad (k = 1, 2, \ldots, n), \quad (2)$$

where $c_k = \rho_k/\rho$ is the mass fraction of component k, with ρ the total density $\Sigma_k \rho_k$ and where

$$\mathbf{J}_k = \rho_k(\mathbf{v}_k - \mathbf{v}), \quad (k = 1, 2, \ldots, n) \quad (3)$$

is the diffusion flow of k, counted with respect to the centre of gravity velocity $\mathbf{v}$, which is defined by $\rho \mathbf{v} = \Sigma_k \rho_k \mathbf{v}_k$. The time derivative in (2) is the "barycentric" substantial derivative $\partial/\partial t + \mathbf{v} \cdot \mathrm{grad}$.

(b) *Conservation of momentum* is given by the equation

$$\frac{\partial \rho \mathbf{v}}{\partial t} = -\mathrm{Div}\, (\rho \mathbf{v}\mathbf{v} + \boldsymbol{P}), \quad (4)$$

where $\rho \mathbf{v}$ is the momentum density. The momentum flux at the right-hand side contains the dyad $\mathbf{v}\mathbf{v}$ (a tensor with α, β components $v_\alpha\, v_\beta$ where α and β are x, y or z) and the pressure tensor $\boldsymbol{P}$. Equation (4) is mathematically equivalent with the equation of motion in a continuous medium

$$\rho \frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = -\mathrm{Div}\, \boldsymbol{P}. \quad (5)$$

We have supposed here that no external forces act on the system (cf. however section 5).

One finds a balance equation for the kinetic energy by scalar multiplication of (5) by $\mathbf{v}$

$$\rho \frac{\mathrm{d}\frac{1}{2}\mathbf{v}^2}{\mathrm{d}t} = -\mathbf{v} \cdot \mathrm{Div}\, \boldsymbol{P} = -\mathrm{div}\, \boldsymbol{P} \cdot \mathbf{v} + \tilde{\boldsymbol{P}} : \mathrm{Grad}\, \mathbf{v}, \quad (6)$$

where $\tilde{\boldsymbol{P}}$ is the transposed matrix of $\boldsymbol{P} (\tilde{P}_{\alpha\beta} = P_{\beta\alpha})$.

Similarly a balance equation for (external) angular momentum per unit mass $\mathbf{L} \equiv \mathbf{x} \wedge \mathbf{v}$ follows by vectorial multiplication of (5) by $\mathbf{v}$:

$$\rho \frac{\mathrm{d}L_{\alpha\beta}}{\mathrm{d}t} = -\sum_\gamma \frac{\partial}{\partial x_\gamma} (x_\alpha P_{\gamma\beta} - x_\beta P_{\gamma\alpha}) + P_{\alpha\beta} - P_{\beta\alpha}, \ (\alpha, \beta = x, y, z). \quad (7)$$

For convenience we have here represented the axial vector $\mathbf{L}$ by an antisymmetric tensor according to the usual convention $L_x \equiv L_{yz} = -L_{zy}$ (cycl.). The summation over γ extends over x, y and z.

(c) *Conservation of angular momentum* is expressed by the equation

$$\rho \frac{\mathrm{d}J_{\alpha\beta}}{\mathrm{d}t} = -\sum_\gamma \frac{\partial}{\partial x_\gamma} (x_\alpha P_{\gamma\beta} - x_\beta P_{\gamma\alpha}), \quad (8)$$

where $\mathbf{J}$ (again representing this axial vector by an antisymmetric tensor) is the angular momentum per unit mass. We split it into an external angular momentum $\mathbf{L}$ and an internal angular momentum $\mathbf{S}$. The balance equation for the latter is obtained by subtraction of (7) from (8), which yields

$$\rho \frac{\mathrm{d}\mathbf{S}}{\mathrm{d}t} = -2\mathbf{P}^a, \quad (9)$$

where $\mathbf{P}^a$ is the antisymmetric part $\frac{1}{2}(\boldsymbol{P} - \tilde{\boldsymbol{P}})$ of the pressure tensor $\boldsymbol{P}$, written as an axial vector. One can write $\mathbf{S}$ as $\boldsymbol{\Theta}\,\boldsymbol{\omega}$, with $\boldsymbol{\Theta}$ the moment of inertia per unit mass and $\boldsymbol{\omega}$ the angular velocity. Then the local rotational energy per unit mass is $u_r = \frac{1}{2}\boldsymbol{\Theta}\boldsymbol{\omega}^2$, for which one finds a balance equation from (9):

$$\rho \frac{\mathrm{d}u_r}{\mathrm{d}t} = -2\omega \cdot \mathbf{P}^a. \tag{10}$$

(d) *Conservation of energy* is expressed by

$$\rho \frac{\mathrm{d}e}{\mathrm{d}t} = -\operatorname{div}(\boldsymbol{P} \cdot \mathbf{v} + \mathbf{J}_q), \tag{11}$$

where e is the total energy per unit mass and $\mathbf{J}_q$ the heat flow. If we define the internal energy u by splitting e in the following way

$$e = \tfrac{1}{2}\mathbf{v}^2 + u_r + u, \tag{12}$$

we can obtain the balance equation for u by subtracting (6) and (10) from (11):

$$\rho \frac{\mathrm{d}u}{\mathrm{d}t} = -\widetilde{\boldsymbol{P}} : \operatorname{Grad} \mathbf{v} + 2\mathbf{P}^a \cdot \omega - \operatorname{div} \mathbf{J}_q. \tag{13}$$

Let us now split the pressure tensor in the following way

$$\boldsymbol{P} = p\boldsymbol{U} + \boldsymbol{\Pi}, \tag{14}$$

where p is the equilibrium pressure ($\boldsymbol{U}$ is the unit matrix), and where $\boldsymbol{\Pi}$ is called the viscous pressure tensor. We can split the latter into three parts

$$\boldsymbol{\Pi} = \Pi\boldsymbol{U} + \mathring{\boldsymbol{\Pi}}^s + \boldsymbol{\Pi}^a, \tag{15}$$

where Π is one third of the trace, $\mathring{\boldsymbol{\Pi}}^s$ is the symmetric part with zero trace and $\boldsymbol{\Pi}^a$ the antisymmetric part. The latter, which according to (14) and (15) is equal to $\boldsymbol{P}^a$, can again be represented by an axial vector $\mathbf{P}^a$. Similarly we can split the velocity gradient tensor

$$\operatorname{Grad} \mathbf{v} = \tfrac{1}{3}(\operatorname{div} \mathbf{v})\,\boldsymbol{U} + (\text{Gråd}\ \mathbf{v})^s + (\operatorname{Grad} \mathbf{v})^a, \tag{16}$$

where the antisymmetric part corresponds to the axial vector $\frac{1}{2}\operatorname{rot} \mathbf{v}$. The balance equation for the internal energy (13) can now be written as

$$\rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + p\frac{\mathrm{d}v}{\mathrm{d}t}\right) = -\Pi \operatorname{div} \mathbf{v} - \mathring{\boldsymbol{\Pi}}^s : (\text{Gråd}\ \mathbf{v})^s - \Pi^a \cdot (\operatorname{rot} \mathbf{v} - 2\omega) - \operatorname{div} \mathbf{J}_q. \tag{17}$$

Here $v \equiv \rho^{-1}$ is the specific volume, and use has been made of the fact that, according to (1), $\mathrm{d}v/\mathrm{d}t$ is equal to $\rho^{-1} \operatorname{div} \mathbf{v}$. This result represents the first law of thermodynamics for our system.

3. ENTROPY LAW AND ENTROPY BALANCE

For the system considered we can express the entropy per unit mass s in terms of the local internal energy, specific volume and mass fractions: $s = s(u, v, c_k)$. We shall assume that locally s is the same function of these variables as it is in equilibrium i.e. more specifically we assume that Gibbs' entropy law is valid along the line of motion of the centre of gravity of a mass element:

$$T\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}t} + p\frac{\mathrm{d}v}{\mathrm{d}t} - \Sigma_k\mu_k\frac{\mathrm{d}c_k}{\mathrm{d}t}, \tag{18}$$

where μ_k is called the chemical potential of component k. If we substitute the mass law (2) and the energy law (17) into this equation we obtain a balance equation for the entropy, which has the form

$$\rho\frac{\mathrm{d}s}{\mathrm{d}t} = -\operatorname{div} \mathbf{J}_s + \sigma, \tag{19}$$

with an "entropy flow"

$$\mathbf{J}_s = (\mathbf{J}_q - \Sigma_k\mu_k\mathbf{J}_k)/T \tag{20}$$

and an "entropy production"

$$\left.\begin{aligned} \sigma = -\mathbf{J}_q \cdot \frac{\operatorname{grad} T}{T^2} - \sum_k \mathbf{J}_k \cdot \operatorname{grad}\left(\frac{\mu_k}{T}\right) \\ -\frac{\Pi \operatorname{div} \mathbf{v}}{T} - \frac{\mathring{\boldsymbol{\Pi}}^s : (\text{Gråd}\ \mathbf{v})^s}{T} \\ -\frac{\Pi^a \cdot (\operatorname{rot} \mathbf{v} - 2\omega)}{T} \geqslant 0. \end{aligned}\right\} \tag{21}$$

According to (19) the entropy can change in two ways: in the first place by external *supply of heat or matter* as expressed by the first term on the right-hand side, which contains the heat flow $\mathbf{J}_q$ and the diffusion flow $\mathbf{J}_k$, as (20) shows. In the second place the entropy can change by *internal production* σ. This entropy production, which is the second term on the right-hand side of (19), is positive (or zero) according to the second law of thermodynamics. It is a measure for the irreversibility of the processes which take place inside the system. (In particular it vanishes at thermodynamic equilibrium.) As its expression (21) shows, it contains five contributions of which the first arises from heat conduction, the second from diffusion of matter and the other three from viscous flow. Each term is the product of a flux (heat flow $\mathbf{J}_q$, diffusion flow $\mathbf{J}_k$, viscous pressure tensor components) and a so-called "thermodynamic force" (temperature gradient, gradient of chemical potential, velocity gradients). It may be noted here already that the first two fluxes and thermodynamic forces are (polar) vectors, the third term contains scalars, the fourth symmetric tensors with zero trace and the fifth axial vectors. We may also remark that we shall see in section 6 that the last three terms of (21) are connected to volume viscosity, shear viscosity and rotational viscosity respectively.

4. CHEMICAL REACTIONS AND RELAXATION PHENOMENA

If a chemical reaction can occur, we must slightly modify the preceding formalism. In the mass laws (1) and (2) we must add a source term at the right-hand side, which accounts for the chemical production of component k in mass per unit volume and unit time. We can write this term as $\nu_k J_c$ where ν_k divided by the molecular mass M_k of k is the stoichiometric coefficient of k in the chemical reaction, and where J_c is called the chemical reaction rate. The latter quantity can alternatively be written as $\rho \mathrm{d}\xi_c/\mathrm{d}t$, where ξ_c is called the chemical "progress variable". In this way (2) becomes

$$\rho \frac{\mathrm{d}c_k}{\mathrm{d}t} = -\operatorname{div} \mathbf{J}_k + \nu_k \rho \frac{\mathrm{d}\xi_c}{\mathrm{d}t}, \quad (k = 1, 2, \ldots, n). \tag{22}$$

Summation over k yields the same equation as before, because, since the total mass is conserved in a chemical reaction, one has $\Sigma_k \nu_k = 0$.

The entropy balance follows now from (18) with (17) and (22). One obtains (19) with (20) for the entropy flux, but in the entropy production (21) an additional term appears:

$$\sigma_c = -\frac{\rho}{T}\frac{\mathrm{d}\xi_c}{\mathrm{d}t}\Sigma_k \mu_k \nu_k = -\frac{\rho}{T}\frac{\mathrm{d}\xi_c}{\mathrm{d}t} A_c, \tag{23}$$

where A_c, defined as $\Sigma_k \mu_k \nu_k$, is called the chemical affinity. The generalization to the case of more than one single chemical reaction is straightforward: one simply obtains sums over chemical reactions in the last term of (22) and in (23).

The occurrence of relaxation processes in a system gives rise to terms in the entropy production similar to those arising from chemical reactions. If a relaxation phenomenon takes place, this means that some "internal state variable" ξ is needed to describe the system. Then the entropy s depends not only on u, v and c_k but also on the internal variable ξ. (The generalization to several internal variables, i.e. to several relaxation processes, is again straightforward.) The Gibbs' entropy law (18) becomes in this way

$$T\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}t} + p\frac{\mathrm{d}v}{\mathrm{d}t} - \Sigma_k \mu_k \frac{\mathrm{d}c_k}{\mathrm{d}t} - A\frac{\mathrm{d}\xi}{\mathrm{d}t}, \tag{24}$$

where A is called relaxation affinity. The entropy production contains therefore an additional term, arising from relaxation,

$$\sigma_r = -\frac{\rho}{T}\frac{\mathrm{d}\xi}{\mathrm{d}t}A, \tag{25}$$

completely analogous to (23). That this must be so is clear because we can consider a chemical reaction as a special case of a relaxation phenomenon.

5. THE CASE OF EXTERNAL FORCES

In the presence of external forces, a source term has to be added in the right-hand side of the equation of motion (5) of the form $\Sigma_k \rho_k \mathbf{F}_k$, where $\mathbf{F}_k$ is the force per unit mass acting on substance k. This means that the balance of kinetic energy is modified, since it is derived from the equation of motion. In the case of *conservative forces* defined as

$$\mathbf{F}_k = -\operatorname{grad} \psi_k, \quad (\text{with } \partial\psi_k/\partial t = 0), \tag{26}$$

one can easily derive a balance equation for the potential energy per unit mass $\psi = \Sigma_k c_k \psi_k$. The internal energy u is now defined by subtracting not only the kinetic energies $\frac{1}{2}\mathbf{v}^2$ and u_r from the total energy e, but also the potential energy ψ. Then one obtains, proceeding in the same way as above, an extra term in the entropy production of the form

$$\sigma_F = \frac{1}{T}\Sigma_k \mathbf{J}_k \cdot \mathbf{F}_k, \tag{27}$$

which can be combined with the diffusion term because it also contains the diffusion flows $\mathbf{J}_k$.

Let us write down also the results for a system in the presence of *non-conservative forces*. The most important example of such forces is that of electromagnetic forces, for which one has the Lorentz expression

$$\mathbf{F}_k = z_k(\mathbf{E} + c^{-1}\mathbf{v}_k \wedge \mathbf{B}), \qquad (28$$

where z_k is the electric charge per unit mass of component k, and where $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic fields. The procedure, outlined above (one must now also establish balances of electromagnetic momentum and energy by means of Maxwell's equations), leads to a new term in the entropy production

$$\sigma_L = \frac{1}{T}\mathbf{i} \cdot \left(\mathbf{E} + \frac{\mathbf{v}}{c} \wedge \mathbf{B}\right), \tag{29}$$

where $\mathbf{i} = \Sigma_k z_k \mathbf{J}_k$ is the conduction current of electricity. In the preceding we have supposed that the material is not polarizable, i.e. we have supposed that the electric and magnetic polarizations per unit mass $\mathbf{p}$ and $\mathbf{m}$ vanish. If this is not the case one has the additional state variables $\mathbf{p}$ and $\mathbf{m}$, and the form of the entropy law becomes

$$T\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}t} + p\frac{\mathrm{d}v}{\mathrm{d}t} - \mathbf{E} \cdot \frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} - \mathbf{B} \cdot \frac{\mathrm{d}\mathbf{m}}{\mathrm{d}t} - \Sigma_k \mu_k \frac{\mathrm{d}c_k}{\mathrm{d}t}. \tag{30}$$

The calculation now leads finally to two more terms in the entropy production:

$$\sigma_p = \frac{\rho}{T}\left(\Delta\mathbf{E}' \cdot \frac{\mathrm{d}\mathbf{p}'}{\mathrm{d}t} + \Delta\mathbf{B}' \cdot \frac{\mathrm{d}\mathbf{m}'}{\mathrm{d}t}\right), \tag{31}$$

where primed quantities are the fields and polarizations measured by an observer with velocity $\mathbf{v}$. The quantities $\Delta\mathbf{E}'$ and $\Delta\mathbf{B}'$ are the deviations of the values of the actual fields from their equilibrium values, which would correspond to the polarizations $\mathbf{p}$ and $\mathbf{m}$. The two terms of (31) are related to the irreversible phenomena of electric and magnetic relaxation.

6. THE PHENOMENOLOGICAL EQUATIONS, THE CURIE PRINCIPLE AND THE ONSAGER RELATIONS

At thermodynamic equilibrium the thermodynamic forces are zero according to the well-known rules of thermodynamics. In conformity with the concept of equilibrium we assume that simultaneously also the fluxes vanish. It is then plausible to make the assumption that, in the first approximation, outside equilibrium the components of the fluxes are linearly related to the components of the thermodynamic forces. Such relations, which are called the phenomenological equations, have been empirically verified for a large class of irreversible processes.

According to their transformation properties under rotations and inversions, we subdivided the different fluxes and thermodynamic forces into scalars, polar vectors, axial vectors and symmetric tensors with zero trace. Now the symmetry properties of the system influence the linear laws in the sense that not all fluxes couple with all thermodynamic forces. This statement, which is known as the *Curie principle*, can be proved for any type of symmetry by means of the theory of invariants [3]. For isotropic systems the result is that a certain force cannot give rise to a flow of different tensorial character. We shall write down the phenomenological equations for the fluxes and thermodynamic forces of (21) which we first rewrite, eliminating $\mathbf{J}_n$ by means of the relation $\Sigma_{k=1}^{n} \mathbf{J}_k = 0$ which results from (3), in the following fashion

$$\sigma = -\mathbf{J}_q \cdot \frac{\operatorname{grad} T}{T} - \sum_{k=1}^{n-1} J_k \cdot \operatorname{grad} \frac{\mu_k - \mu_n}{T} - \frac{\Pi \operatorname{div} \mathbf{v}}{T} - \frac{\overset{\circ}{\Pi}{}^{s} : (\mathrm{Gr\mathring{a}d}\,\mathbf{v})^{s}}{T} - \frac{\Pi^{a} \cdot (\operatorname{rot} \mathbf{v} - 2\omega)}{T}. \tag{32}$$

Then, according to what was said above, we have the phenomenological equations:

$$\mathbf{J}_q = -L_{qq}\frac{\operatorname{grad} T}{T^2} - \sum_{k=1}^{n-1} L_{qk} \operatorname{grad} \frac{\mu_k - \mu_n}{T}, \tag{33}$$

$$\mathbf{J}_i = -L_{iq}\frac{\mathrm{grad}\,T}{T^2} - \sum_{k=1}^{n-1} L_{ik}\,\mathrm{grad}\frac{\mu_k - \mu_n}{T},$$

$$(i = 1, 2, \ldots, n-1), \qquad (34)$$

$$\Pi = -L_v\frac{\mathrm{div}\,\mathbf{v}}{T} \equiv -\eta_v\,\mathrm{div}\,\mathbf{v}, \qquad (35)$$

$$\mathring{\Pi}^s = -L\frac{(\mathrm{Gr\mathring{a}d}\,\mathbf{v})}{T} \equiv -2\eta\,(\mathrm{Gr\mathring{a}d}\,\mathbf{v})^s, \qquad (36)$$

$$\Pi^a = -L_r\frac{\mathrm{rot}\,\mathbf{v} - 2\omega}{T} \equiv -\eta_r(\mathrm{rot}\,\mathbf{v} - 2\omega). \qquad (37)$$

Equations (33) and (34) contain vectorial fluxes and forces, (35) scalars, (36) symmetric tensors with zero trace, and (37) axial vectors.

All coefficients have a particular physical meaning. Thus L_{qq}/T^2 is the heat conductivity, the L_{iq} are related to the thermal diffusion coefficients, the L_{qi} are related to the Dufour coefficients, the L_{ik} are related to the diffusion coefficients, η_v is the volume viscosity, η is the shear viscosity and η_r is the rotational viscosity. With the help of some transformations which leave the entropy production invariant one can introduce diffusion flows which are counted with respect to other reference velocities as the centre of gravity velocity $\mathbf{v}$, employed here. The gradients of the chemical potentials can alternatively be expressed in terms of various composition parameters such as the mass fractions c_k, the molar fractions, partial densities and the like. It is possible to develop in this way a completely rigorous theory of diffusion coefficients for any number n of chemical components [3].

If a relaxation phenomenon (or a chemical reaction) occurs, we have the additional term (25) in the entropy production. Since it is a product of scalars, we must consider it together with the volume viscosity term; this yields the phenomenological equations:

$$\Pi = -L_v\frac{\mathrm{div}\,\mathbf{v}}{T} - L_{vr}\frac{\rho}{T}A, \qquad (38)$$

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = -L_{rv}\frac{\mathrm{div}\,\mathbf{v}}{T} - L_r\frac{\rho}{T}A. \qquad (39)$$

We have again the volume viscosity $\eta_v = L_v/T$ and furthermore a relaxation coefficient L_r, which can be connected to a characteristic time because we can write for (39), omitting for the moment the term with div $\mathbf{v}$,

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = -L_r\frac{\rho}{T}A = -L_r\frac{\rho}{T}\frac{\partial A}{\partial \xi}(\xi - \xi_0), \qquad (40)$$

where ξ_0 is the equilibrium value of ξ. This equation shows that

$$\tau \equiv \frac{T}{L_r\rho}\frac{\partial \xi}{\partial A} \qquad (41)$$

is a characteristic time, called the relaxation time. Finally we have in (38) and (39) two cross-coefficients L_{rv} and L_{vr}.

If external forces act on the system, we have according to (27) a term $\mathbf{F}_k/T$ besides the original thermodynamic force $-\mathrm{grad}\,(\mu_k/T)$. If, for example, $\mathbf{F}_k$ is the centrifugal force, then we can derive the theory of sedimentation in rotating systems. If $\mathbf{F}_k$ is of electromagnetic origin, then the theory of electric conduction, of galvanomagnetic and thermomagnetic phenomena and of electric and magnetic relaxation can be developed.

Another simplification of the scheme of coefficients can be obtained with the help of the *Onsager reciprocal relations*, which play a central role in non-equilibrium thermodynamics. These relations can be derived with the help of statistical mechanical notions from the property of "time reversal invariance" (or "microscopic reversibility") of the microscopic mechanical laws (i.e. invariance for $t \longleftrightarrow -t$). In the cases considered here the Onsager relations read then

$$L_{iq} = L_{qi} \qquad (i = 1, 2, \ldots, n-1), \qquad (42)$$

$$L_{ik} = L_{ki}, \qquad (i, k = 1, 2, \ldots, n-1), \qquad (43)$$

$$L_{vr} = -L_{rv}. \qquad (44)$$

Relation (42) connects the thermal diffusion coefficient and the Dufour coefficient. Relation (43) is a connexion between diffusion coefficients. For binary mixtures ($n = 2$) there is only one coefficient L_{11} and thus no Onsager relation; for ternary mixtures ($n = 3$) one has four coefficients L_{11}, L_{12}, L_{21} and L_{22}, with one Onsager relation $L_{12} = L_{21}$ of the type (43). The minus sign in (44) is a consequence of the fact that, whereas A is a so-called even variable (its sign does not change when the individual particle velocities are reversed), the force div $\mathbf{v}$ has odd character with respect to particle velocity reversal.

(We shall not consider here the case of external magnetic fields, where the form of the Onsager relations is slightly modified.)

7. THE DIFFERENTIAL EQUATIONS

If the phenomenological equations (33)–(37) are substituted into the $n - 1$ conservation laws for matter (2) and $\partial\rho/\partial t = -\operatorname{div}\rho\mathbf{v}$ (which follows from (1) by summation over k), the equation of motion (5), the equation of internal angular momentum (9) and the equation of internal energy (17), one obtains a set of $n + 7$ partial differential equations for the $n + 7$ independent variables: the mass fractions $c_1, c_2, \ldots, c_{n-1}$, the density ρ, the cartesian components of $\mathbf{v}$ and ω, and the temperature T. The equations of state allow one to express the equilibrium pressure p, the energy u and the chemical potentials μ_k, occurring in the equations, in terms of those independent variables. The set of equations, established in this way, describes completely the time behaviour of the system for specified initial and boundary conditions.

For a one-component isotropic fluid the differential equations become, in the way outlined above,

$$\frac{\partial\rho}{\partial t} = -\operatorname{div}\rho\mathbf{v}, \tag{45}$$

$$\rho\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = -\operatorname{grad}p + \eta\Delta\mathbf{v} + (\tfrac{1}{3}\eta + \eta_v)\operatorname{grad}\operatorname{div}\mathbf{v} + \eta_r\operatorname{rot}(2\omega - \operatorname{rot}\mathbf{v}), \tag{46}$$

$$\frac{\mathrm{d}\omega}{\mathrm{d}t} = -\frac{4\eta_r}{\rho\Theta}(\omega - \tfrac{1}{2}\operatorname{rot}\mathbf{v}), \tag{47}$$

$$\rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + p\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \eta_v(\operatorname{div}\mathbf{v})^2 + 2\eta\,(\mathring{\mathrm{Grad}}\,\mathbf{v})^s : (\mathring{\mathrm{Grad}}\,\mathbf{v})^s + \eta_r(\operatorname{rot}\mathbf{v} - 2\omega)^2 + \lambda\Delta T. \tag{48}$$

We have supposed here that the phenomenological coefficients, the three viscosities η_v, η and η_r, and the heat conductivity λ, are constants. These equations, which are the conservation of mass law (45), the equation of motion (46), the internal angular momentum law (47) and the internal energy balance (48), must be supplemented by the equations of state

$$p = p(\rho, T), \tag{49}$$

$$u = u(\rho, T). \tag{50}$$

The set of equations (45)–(50) describes the general "thermohydrodynamic" behaviour of an isotropic fluid. It contains as a special case ordinary hydrodynamics which is based on (45)–(48) alone by assuming that either isothermal or adiabatic conditions are fulfilled. In both cases p is a function of ρ only, so that the hydrodynamic behaviour is already given by (45)–(47), if $p = p(\rho)$ is substituted. We note that (46) is the well-known Navier–Stokes equation, supplemented by a rotational term, and that the first two terms of the right-hand side of (48) are the Rayleigh dissipation function. The complete set of equations contains also the theory of heat conduction. In particular equation (48) becomes Fourier's differential equation for a system at rest:

$$\rho\frac{\partial u}{\partial t} = \lambda\Delta T, \tag{51}$$

where $\partial u/\partial t = c_v\partial T/\partial t$ with c_v the specific heat per unit mass.

If a chemical reaction occurs we need the phenomenological equations (38) and (39), and the mass law (22) instead of (2).

If a relaxation process takes place we need also the phenomenological equations (38) and (39), but as a mass law equation (2). A new equation of state is required besides the others, mentioned above, which gives the affinity A in terms of the independent state variables, amongst which ξ now occurs. One can also develop the theory of sound dispersion and absorption, caused by a relaxation process and by heat conduction and viscous flow, with the help of the complete set of equations. The important result can then be derived that for sound frequencies ν such that

$\nu\tau \ll 1$, where τ is the relaxation time (41), the relaxation phenomenon can formally be described as an effective volume viscosity.

As indicated in the beginning of this section, for multi-component systems, where diffusion occurs, the set of differential equations becomes more complicated. It may be said that non-equilibrium thermodynamics permits one to study various irreversible processes as heat conduction, diffusion of matter and viscous flow from a single point of view. It encompasses a number of phenomenological theories such as the hydrodynamics of viscous fluids, the theory of diffusion and the theory of heat conduction.

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Résumé—"La thermodynamique en non-équilibre" peut servir de base pour un traitement macroscopique des phénomènes irréversibles. On montre que, pour un système dans lequel la conduction thermique, la diffusion, l'écoulement visqueux etc. peuvent intervenir, on peut trouver unsustème complet d'équations différentielles décrivant le comportement irréversible, à partir des lois de conservation, de l'équilibre d'entropie et des équations décrivant le phénomène.

Zusammenfassung—Die "Nicht-Gleichgewichts-Thermodynamik" kann als Grundlage für die makroskopische Behandlung irreversibler Vorgänge dienen. Für ein System, in welchem Wärmeleitung, Diffusion, zähe Strömung usw. vor sich gehen kann, wird gezeigt, wie man einen vollständigen Satz von Differentialgleichungen zur Beschreibung des irreversiblen Verhaltens findet, indem man von den zugehörigen Erhaltungssätzen, der Entropiebilanz und phänomenologischen Gleichungen ausgeht.

Аннотация—«Неравновесная термодинамика» может служить основой для макроскопического исследования необратимых явлений переноса. Для системы, в которой имеют место явления переноса: теплопроводность, диффузия, вязкое течение и другие, выведена полная система дифференциальных уравнений, описывающая все виды переноса в их взаимосвязи. Эта система уравнений получена на основе законов сохранения, уравнения баланса знтрении и феноменологических уравнений.