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ON THE NATANSON PRINCIPLE OF IRREVERSIBLE PROCESSES

By K. Gumiński

Department of Theoretical Chemistry, Institute of Chemistry, Jagellonian University, Cracow*

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It is shown that Natanson's principle in its generalized form is a most general principle of dissipative phenomena containing as a special case the well known linear theory of irreversible thermodynamics and potentially comprising possible non-linear theories as well.

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Eighty years ago (1896) W. Natanson published a paper "On the Laws of Irreversible Processes" [1]. He proposed for these processes a new variational principle as a generalization of the well known Hamiltonian principle. He called it the "Thermokinetic Principle" and expressed it in the following form

$$\int_{t_0}^{t_1} dt(\delta\mathcal{T}-\delta\mathcal{U}+\sum_i P_i\delta q_i+\delta Q) = 0. \tag{1}$$

Natanson's assumptions were the following.

The state of the system is determined by independent variables q_i and their time derivatives $s_i = \frac{d}{dt} q_i$. The variables q_i are quite general; for instance, one of them can be the temperature. Thus q_i's can be generalized mechanical coordinates of the system as well as thermodynamic parameters, describing the internal state.

$\mathcal{T}$ is postulated to be a function of q_i's and a homogeneous function of the second order of s_i's. Hence we can assume $\mathcal{T}$ to be composed additively of the kinetic energy of the system as a whole, $\mathcal{T}_M$, and of Θ, a function of the thermodynamic parameters and a homogeneous function of the second order of their time derivatives.

$\mathcal{U}$ is postulated to be a function of q_i's only. Hence we can assume it to be composed additively of the potential energy of the system as a whole, $\mathcal{U}_M$, and of its internal energy, U.

$\sum_i P_i\delta q_i$ means a variation of the reversible work, where P_i is the "generalized force" acting on the "displacement" δq_i.

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* Address: Zakład Chemii Teoretycznej, Instytut Chemii UJ, Karasia 3, 30-060 Kraków, Poland.

The term δQ denotes a variation of the energy exchanged as heat irreversibly with the surrounding. Thus from the second law of thermodynamics we have

$$\delta Q = \delta Q^0 - \delta Q', \tag{2}$$

where δQ^0 is the variation of the reversible heat and $\delta Q'$ of the "uncompensated heat" of Clausius.

Natanson has shown that from his principle follow: the principle of energy conservation, the reversible dynamics, the concept of free energy, the reversible thermodynamics, the irreversible dynamics, the irreversible hydrodynamics, the diffusion, the heat conductivity, the irreversible electromagnetic phenomena and the dissipation of electromagnetic energy.

However the idea of Natanson has not been taken up by contemporary science.

It was only in the thirtieth of this century that the problem of irreversibility became the subject of investigations. Based on the papers of Onsager, Machlup, Prigogine, Glansdorff, De Groot, the new thermodynamics of irreversible processes was developed. In the last twenty years some new variational principles have been proposed. These are: the Onsager and Machlup principle of minimum dissipation of energy, the Prigogine principle of minimum production of entropy in a stationary state, the Gyarmati principle of dissipative processes and the equivalent Vojta's principle.

The principle of Gyarmati [2, 3] which is a generalization of the principles of Onsager, Machlup and Prigogine, has the form

$$\delta \int_V (\sigma - \psi) dV = 0, \tag{3}$$

where the lagrangian density $\mathscr{L}$ is a function of the local intensive parameters, Γ_i, and of their local gradients, $\nabla \Gamma_i$,

$$\mathscr{L} = \sigma - \psi = \mathscr{L}(\Gamma_i, \nabla \Gamma_i), \tag{4}$$

and where the local production of entropy is given by

$$\sigma = \sum_{i=1}^{f} X_i J_i. \tag{5}$$

In this equation $X_i \equiv \nabla \Gamma_i$ denotes the local thermodynamic force and J_i the local conjugated thermodynamic flux. The local "dissipation potential" ψ is defined as

$$\psi \equiv \tfrac{1}{2} \sum_{i,k=1}^{f} L_{i,k} X_i X_k. \tag{6}$$

In a linear theory the "phenomenological coefficients" L_{ik} are constant

$$L_{i,k} = \text{const.} \tag{7}$$

and the kinematic equations

$$J_i = \sum_{k=1}^{f} L_{i,k} X_k, \tag{8}$$

$$X_i = \sum_{k=1}^{f} R_{i,k} J_k \tag{9}$$

are valid. The matrices L_{ik} and R_{ik} are mutually reciprocal and the Onsager–Casimir relations

$$L_{ik} = \varepsilon_i \varepsilon_k L_{ki}; \qquad \varepsilon_i, \varepsilon_k = \pm 1 \tag{10}$$

are fulfilled. Then we have

$$\sigma = \sum_{i,k=1}^{f} L_{ik} X_i X_k = \sum_{i,k=1}^{f} R_{ik} J_i J_k. \tag{11}$$

The Euler–Lagrange equations following from the principle (3) are

$$\nabla \cdot \frac{\partial \mathscr{L}}{\partial \nabla \Gamma_i} - \frac{\partial \mathscr{L}}{\partial \Gamma_i} = 0 \qquad (i = 1, 2, \ldots, f). \tag{12}$$

From these equations the transport and kinematic equations can be deduced.

On the other hand, the Vojta principle [3, 4] has the form

$$\delta \int_{t_1}^{t_2} (\sigma - \Phi) dt = 0, \tag{13}$$

where the thermodynamic lagrangian functional $\mathscr{L}$ depends on the state fields, $\alpha_i(r, t)$, which are intensive state variables (e.g densities) derived from extensive variables, and on their time derivatives, $\dot{\alpha}_i$

$$\mathscr{L} = \sigma - \Phi = \mathscr{L}(\alpha_i, \dot{\alpha}_i). \tag{14}$$

In this equation the entropy production functional is given by

$$\sigma = -\sum_i \sum_k \int_V \int_V s_{ik}(r, r') \alpha_i(r, t) \dot{\alpha}_k(r', t) dr dr', \tag{15}$$

where

$$s_{ik} = -\left. \frac{\delta^2 \int \{\alpha_j(r'', t)}{\delta \alpha_i(r, t) \delta \alpha_k(r', t)} \right|_{\alpha_i(r,t) \equiv 0, \ \alpha_k(r',t) \equiv 0}. \tag{16}$$

The "dissipation potential" functional, Φ, is defined as

$$\Phi \equiv \tfrac{1}{2} \sum_i \sum_k \int_V \int_V R_{ik}(r, r') \dot{\alpha}_i(r, t) \dot{\alpha}_k(r', t) dr dr', \tag{17}$$

where $R_{ik}(r, r')$ are the generalized phenomenological coefficients.

The Euler–Lagrange equations following from (13) are

$$\frac{\partial}{\partial t} \frac{\delta \mathscr{L}}{\delta \dot{\alpha}_i} - \frac{\delta \mathscr{L}}{\delta \alpha_i} = 0 \qquad (i = 1, 2, \ldots f). \tag{18}$$

From these equations the same transport and kinematic equations can be derived as those following from (12).

We note, that in the Gyarmati principle we have a volume integral and the operator ∇, whereas in the Vojta principle we have a time integral and the operator $\frac{d}{dt}$.

We see that the dissipative phenomena can be described in the "space" or in the "time" representation. According to Gyarmati's opinion "it should be said that a single variational principle exists and the forms (3) and (13) are only alternative forms of it". This "complementarity" of the phenomenological description of macroscopic phenomena seems to be interesting.

Now let us return to the Natanson principle. Taking the above discussion on Natanson's postulates into account, we can rewrite his principle in the form

$$\int_{t_0}^{t_1} dt(\delta\mathcal{T}_M+\delta\Theta-\delta\mathcal{U}_M-\delta U+\sum_i P_i\delta q_i+\delta Q) = 0. \tag{19}$$

Suppose that the kinetic and potential energies of the system as a whole are not varied. With (2) we have

$$\int_{t_0}^{t_1} dt(\delta\Theta-\delta U+\sum_i P_i\delta q_i+\delta Q^0-\delta Q') = 0. \tag{20}$$

Considering the well known thermodynamic relation

$$\delta U = \sum_i P_i\delta q_i+\delta Q^0, \quad (\delta Q^0 = T\delta S), \tag{21}$$

we have from Eq. (20)

$$\int_{t_0}^{t_1} dt(\delta\Theta-\delta Q') = 0, \tag{22}$$

or

$$\int_{t_0}^{t_1} dt\delta(\Theta-Q') = 0. \tag{23}$$

Natanson's principle was written for global thermodynamic systems or for global phases. In 1896 the local formulations of thermodynamics had not yet been used[1]. Let us now introduce the notations Θ_l and Q_l' for the local quantities of Θ and Q'. We have then $\Theta_l = \Theta_l(r, t)$, $Q_l' = Q_l'(r, t)$ and

$$\Theta = \int_V \Theta_l dV; \quad Q' = \int_V Q_l' dV, \tag{24}$$

where V is the volume of the global system or phase. We have then

$$\int_{t_0}^{t_1} dt\delta[\int_V (\Theta_l-Q_l')dV] = 0. \tag{25}$$

From the physical meaning of the integrand in (23) we see that Q' is the uncompensated heat of Clausius produced in a unit of time. Hence Q_l' is the local dissipation of

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[1] Only analogies between thermodynamics and dynamics but not hydrodynamics were then looked for.

energy in a unit of time and therefore it can be expressed as $T\sigma$, with σ being the local production of entropy. Thus we can write

$$\int_{t_0}^{t_1} dt\delta[\int_V (\Theta_l - T\sigma)dV] = 0. \tag{26}$$

Denoting

$$\Theta'_l \equiv \frac{\Theta_l}{T}, \tag{27}$$

we get

$$\int_{t_0}^{t_1} dt\delta\{\int_V [(\Theta'_l - \sigma)T]dV\} = 0, \tag{28}$$

or

$$\delta \int_{t_0}^{t_1} \{\int_V [(\sigma - \Theta'_l)T]dV\}dt = 0. \tag{29}$$

Now we will generalize this thermokinetic principle. This will be done in two steps. The first of them is related to the classical field theory applied to the thermodynamics of continuous systems. We postulate namely, that Θ'_l is a function of the thermodynamic parameters and a homogeneous function of the second order of their derivatives with respect to time $\left(\frac{d}{dt}\right)$ or with respect to the space coordinates (∇).

The second step goes further. We abandon the restriction of the postulate of homogeneity and second order of the function Θ'_l and postulate only that Θ'_l is a function of thermodynamic parameters and of their derivatives with respect to time or with respect to space coordinates.

We will name this generalized thermokinetic principle the generalized Natanson principle.

Now, if this generalized principle is applied in the special case where Θ'_l is a function of thermodynamic parameters and a homogeneous function of the second order of their derivatives with respect to time or with respect to the space coordinates, then we can take, for instance, for $\int_V \sigma T dV$ the equation

$$\sigma^* = -\sum_i \sum_k \int_V \int_V s_{i,k}(r, r')\alpha_i(r, t)\dot{\alpha}_k(r', t)T(r, t)drdr' \tag{30}$$

following from (15) and form $\int_V \Theta'_l T dV$ the equation

$$\Phi^* = \tfrac{1}{2}\sum_i \sum_k \int_V \int_V R_{i,k}(r, r')\dot{\alpha}_i(r, t)\dot{\alpha}_k(r', t)T(r, t)drdr' \tag{31}$$

following from (17). Then from (29) we obtain

$$\delta \int_{t_0}^{t_1} [\sigma^* - \Phi^*]dt = 0, \tag{32}$$

that is the Vojta principle in energy representation.

Similarly, taking for σ the Eq. (5) and for Θ' the Eq. (6) we obtain from (29)

$$\delta \int_{t_0}^{t_1} dt \int_V [(\sigma - \psi)T] dV = 0. \tag{33}$$

Hence

$$\delta \int_V [(\sigma - \psi)T] dV = 0, \tag{34}$$

that is the Gyarmati principle in energy representation.

In this special case we obtain also the well known Onsager's linear thermodynamics of irreversible processes.

(We recall that in the case of Vojta's principle we take the quantities α_i and $\dot{\alpha}_i$ as variables, whereas in the case of Gyarmati principle we take Γ_i and $\nabla \Gamma_i$).

However the expressions (17), (6) and (15), (5) are valid under certain conditions only. The expression for production of entropy as a sum of products of forces and fluxes is obtained under the assumption of the validity of the hypothesis of the local equilibrium. The dissipation potentials, as defined in Eqs. (6),(17), confine the theory to the description of linear phenomena with linear kinematic equations, only. It is obvious that for non-linear processes the expressions for dissipation potentials must be generalized and so must be the kinematic equations. It may also happen (in the case of turbulent processes, such as for instance explosive chemical reaction) that expressions (5) and (15) for the production of entropy cease to be valid.

In these cases the validity of the restriction of homogeneity and second order of the function Θ'_i may not be fulfilled. Then the generalized Natanson principle should be applied. Depending on the case at hand different expressions for Θ'_i and σ would then be valid[2].

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[2] In many of such cases the "universal" form of Gyarmati's principle of irreversible processes

$$\delta \int_V [\sigma - (\psi + \varphi)] dV = 0, \tag{35}$$

where

$$\varphi \equiv \frac{1}{2} \sum_{i,k=1}^{f} R_{ik} J_i J_k, \tag{36}$$

or the "universal" form of Vojta's principle

$$\delta \int_{t_1}^{t_2} [\sigma - (\Psi + \Phi)] dt = 0, \tag{37}$$

where

$$\Psi \equiv \frac{1}{2} \sum_i \sum_k \int_V \int_V L_{ik}(r, r') \alpha_i(r, t) \alpha_k(r', t) dr\, dr' \tag{38}$$

may be particularly usefull. We have then in these cases

$$\Theta'_i = \psi + \varphi, \tag{39}$$

or

$$\int_V \Theta'_i T dV = \Psi^* + \Phi^* \tag{40}$$

to be introduced in (29).

We see that the contemporary linear thermodynamics of irreversible processes is already contained in the generalized Natanson principle. However, the generalized Natanson principle may potentially comprise possible non-linear theories as well. Thus the thermokinetic principle of Natanson proposed in 1896 is not only chronologically the first but so far — in its generalized form — a most general variational principle for dissipative processes.

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