ON POSSIBLE FORMULATION OF THE EXTENDED
IRRREVERSIBLE THERMODYNAMICS AND
THE THERMODYNAMICS WITH INTERNAL VARIABLES

Josef Rosenberg*, Miroslava Svobodová*

There exist different formulations of the irreversible thermodynamics. Depending on the distance from the equilibrium state and on the characteristic time the main theories are the classical theory (CIT), the thermodynamics with internal variables (IVT) and the extended theory (EIT). Sometimes it is not easy to choose the proper theory and to use it efficiently with respect to applied problems considering different fields of interest. Especially EIT is explained mainly for very special choice of the dissipative fluxes under specific presumptions. The paper tries to formulate EIT and IVT in a simple, unified but general enough form. The basic presumptions for EIT are shown and discussed, further a possible generalization is proposed. The formulation allows the integration of IVT and EIT even for the mixture of chemically interacting components and diffusion. The application of the formulation is demonstrated on an example.

Keywords: extended irreversible thermodynamics, thermodynamics with internal variables, mixture

1. Introduction

Non-equilibrium thermodynamics is necessary for a suggestion of the mathematical and numerical models of modern materials especially living tissues. The grounds for it are dissipative processes with different relaxation times running in those materials.

Instead of a closed theory a lot of different theories can be found. Let the irreversible thermodynamics with internal variables (IVT) and the extended irreversible thermodynamics (EIT) are considered. Lots of publications are dedicated to both theories, e.g. [4] for IVT and [2],[3],[5] for EIT. The aim of the paper is to point out certain assumptions and advantages of the theories in the particular applications. The attention is mainly dedicated to EIT while IVT was discussed in [7].

According to [5] the application of IVT is limited to processes not far from thermodynamic equilibrium due to the assumption of either local or accompanying equilibrium state of the process. It can not be applied in a situation in which the characteristic relaxation times of the involved irreversible dissipation process (chemical, mechanical, thermal, electric, etc.) and the dynamic characteristic times of interest are of the same order – the Deborah number is close to 1. To bridge the gap EIT introduces the local non-equilibrium state. The thermodynamic fluxes are introduced into the set of state variables. The fluxes describe the interaction of a material point with its neighborhood. Consequently the entropy depends not only on the heat flux but also on these fluxes that can be controllable.

* prof. Ing. J. Rosenberg, DrSc., Ing. M. Svobodová, Faculty of Applied Sciences, University of West Bohemia in Pilsen, Univerzitní 2; 306 14, Plzeň
First, EIT applied to a one component continuum is discussed. Then the generalization to the multicomponent continuum is suggested, the diffusion and chemical reactions are taken into account. The combination of IVT and EIT is shown together with an example at the end of the paper.

2. EIT - one component continuum

Let the entropy $s(u, q, a_i, J_i)$, $i = 1, 2$ be a function of internal energy $u$, heat flux $q$, new fluxes $J_i$, $i=1,2$ and two sets of the state variables $a_i$, $i=1,2$ that need not to be disjunct. Let the internal energy be expressed by the following relation

$$\rho \dot{u} = -\nabla \cdot q + F_{c1} \cdot \dot{a}_1 + F_{c2} \cdot \dot{a}_2 + J_1 \cdot \dot{a}_1 + J_2 \cdot \dot{a}_2 . \tag{1}$$

REMARK: Due to the generalization of the discussed theory the authors warrant to use the notation $\mathbf{A} \cdot \mathbf{B}$ and $\mathbf{A} \times \mathbf{B}$ leading finally to a scalar and a vector value, respectively. Throughout the paper $a$, $A$, $\alpha$ represents a scalar, $\mathbf{a}$, $\mathbf{A}$, $\beta$ or $\mathbf{B}$ a set of either scalars or vectors or tensors, except $\nabla$ is a vector. For e.g. $\mathbf{A} = \{ A_1, A_2, \ldots \}$, $\mathbf{B} = \{ \beta_1, \beta_2, \ldots \}$: $\mathbf{B} \cdot \mathbf{A} = \beta_1 \cdot A_1 + \beta_2 \cdot A_2 + \ldots$ is a scalar, $\mathbf{B} \times \mathbf{A} = \beta_1 \times A_1 + \beta_2 \times A_2 + \ldots$ is a vector, $\mathbf{B} \cdot \mathbf{A} = \{ \beta_1 A_1, \beta_2 A_2, \ldots \}$, $\mathbf{A} \cdot \mathbf{a} = A_1 \cdot a + A_2 \cdot a + \ldots$ are vectors, $\mathbf{A} \times \mathbf{a} = A_1 \times a + A_2 \times a + \ldots$ is a scalar. If e.g. $(\beta_1)_j = f_j$ and $(\mathbf{A})^{kl} = g^{kl}$ then $\beta_1 \times A_1 = f_j g^{kl}$, etc.

Let $F_{c1}$ be the sets of the classical forces producing work in the current space and the last two terms in (1) express the work of the new fluxes. For the entropy can be written

$$\dot{s} = \frac{\partial s}{\partial u} \dot{u} + \frac{\partial s}{\partial q} \cdot \dot{q} + \frac{\partial s}{\partial a_1} \cdot \dot{a}_1 + \frac{\partial s}{\partial a_2} \cdot \dot{a}_2 + \frac{\partial s}{\partial J_1} \cdot \dot{J}_1 + \frac{\partial s}{\partial J_2} \cdot \dot{J}_2 , \tag{2}$$

where

$$\frac{\partial s}{\partial u} = \theta^{-1} , \quad \frac{\partial s}{\partial q} = \theta^{-1} \alpha_q(u, q, J_i, a_i) , \tag{3}$$

$$\frac{\partial s}{\partial a_i} = -\theta^{-1} \rho \cdot F_{ci} , \quad \frac{\partial s}{\partial J_i} = \theta^{-1} \alpha_{J_i}(u, q, J_i, a_i).$$

Here $\theta$ is the ‘irreversible’ temperature differing from $T$ due to the entropy dependence on the additional fluxes.

Inserting (1) and (3) into (2) the following relation is obtained

$$\rho \dot{s} = \theta^{-1} \{ -\nabla \cdot q + (F_{c1} + J_1 - F_{c1}) \cdot \dot{a}_1 + (F_{c2} + J_2 - F_{c2}) \cdot \dot{a}_2 + \rho \alpha_q \cdot \dot{q} + \rho \alpha_{J_1} \cdot \dot{J}_1 + \rho \alpha_{J_2} \cdot \dot{J}_2 \} . \tag{4}$$

The first assumption according to [3] follows

$$\alpha_q = \alpha_{q0} q , \quad \alpha_{J_i} = \alpha_{J_i0} J_i , \quad \theta = T , \tag{5}$$

where $\alpha_{q0}$ and $\alpha_{J_i0}$ are the scalar functions. Then (4) has the form

$$\rho \dot{s} = -\nabla \cdot (T^{-1} q) + q \cdot \nabla (T^{-1}) + T^{-1} [(F_{c1} - F_{c1} + J_1) \cdot \dot{a}_1 + \rho T^{-1} (\alpha_{q0} q \cdot \dot{q} + \alpha_{J_i0} J_1 \cdot \dot{J}_1 + \alpha_{J_20} J_2 \cdot \dot{J}_2) . \tag{6}$$
The entropy source is given according to the general balance equation by

$$\sigma^s = \rho \dot{s} + \nabla \cdot J^s .$$

The flux of the entropy can be supposed according to [5] as

$$J^s = J^s(T, q, J_i, a_i).$$

The polynomial of the second degree is chosen as a function approximation and according to [3] only the terms containing $q$ are selected

$$J^s = T - 1 \dot{q} + (\beta_1 J_1) \cdot q + (\beta_2 J_2) \cdot q .$$

This is the second fundamental assumption. A different form of the entropy flux – it represents different selections from the above mentioned polynomial e.g. [1] – can be found in literature.

Putting (8) into (7) and using (6) the following relation is obtained

$$\sigma^s = q \cdot \left[ \nabla T - 1 + \rho T^{-1} \alpha q_0 \dot{q} + \nabla \cdot (\beta_3 J_1) + \nabla \cdot (\beta_4 J_2) \right] +
+ J_1 \cdot \left( T^{-1} \dot{a}_1 + \rho T^{-1} \alpha J_{10} J_1 + \beta_3 T \nabla q \right) +
+ J_2 \cdot \left( T^{-1} \dot{a}_2 + \rho T^{-1} \alpha J_{20} J_2 + \beta_4 T \nabla q \right) +
+ T^{-1} (F_{c2} - F_{e2}) \cdot \dot{a}_2 + T^{-1} (F_{c1} - F_{e1}) \cdot \dot{a}_1 \geq 0 .$$

The terms in brackets represent the forces

$$X_q = \nabla T - 1 + \rho T^{-1} \alpha q_0 \dot{q} + \nabla \cdot (\beta_3 J_1) + \nabla \cdot (\beta_4 J_2) ,$$

$$X_{J_1} = T^{-1} \dot{a}_1 + \rho T^{-1} \alpha J_{10} J_1 + \beta_3 \nabla q ,$$

$$X_{J_2} = T^{-1} \dot{a}_2 + \rho T^{-1} \alpha J_{20} J_2 + \beta_4 \nabla q ,$$

$$X_{a_1} = T^{-1} \dot{a}_1 ,$$

$$X_{a_2} = T^{-1} \dot{a}_2 ,$$

and further

$$F_{c1} - F_{e1} = F_{\text{dis1}} , \quad F_{c2} - F_{e2} = F_{\text{dis2}} .$$

The inequality (9) is fulfilled e.g. if

$$[X_q, X_{J_1}, X_{J_2}, X_{a_1}, X_{a_2}]^T = L [q, J_1, J_2, F_{\text{dis1}}, F_{\text{dis2}}]^T ,$$

where the superscript $[\ ]^T$ represents the row vector transpose and the matrix of Onsager coefficients $L$ fulfills the proper conditions

$$L_{ii} \geq 0 , \quad L_{ii} L_{jj} \geq \frac{1}{4} (L_{ij} + L_{ji})^2 , \quad i, j = 1, 2, \ldots .$$

They are the linear constitutive equations according to [3].

Let the uncoupled case be considered. The matrix $L$ is diagonal

$$L = \begin{bmatrix}
L_q & 0 & 0 & 0 & 0 \\
0 & L_{J_1} & 0 & 0 & 0 \\
0 & 0 & L_{J_2} & 0 & 0 \\
0 & 0 & 0 & L_{a_1} & 0 \\
0 & 0 & 0 & 0 & L_{a_2}
\end{bmatrix} .$$
where all $L_{ij}$ are non-negative. More general conditions taking into account the coupling between fluxes exist. They are mentioned further in the paper. The choice (12) and the matrix $L$ form (14) are the third fundamental assumption considered in the discussed approach to the theory. Inserting from (10) and (14) into (12) the evolution equations of all fluxes are obtained as follows

$$L_q q = \nabla T^{-1} + \rho T^{-1} \alpha_{0} q \dot{q} + \nabla \odot (\beta_3 J_1) + \nabla \odot (\beta_4 J_2),$$

$$L_{J_1} J_1 = T^{-1} \dot{a}_1 + \rho T^{-1} \alpha_{J_10} J_1 + \beta_3 \nabla q,$$

$$L_{J_2} J_2 = T^{-1} \dot{a}_2 + \rho T^{-1} \alpha_{J_20} J_2 + \beta_4 \nabla q,$$

$$L_{a_1} F_{\text{dis}1} = T^{-1} \dot{a}_1,$$

$$L_{a_2} F_{\text{dis}2} = T^{-1} \dot{a}_2.$$ (15)

Let the free energy $f = u - Ts$ be introduced, then

$$\dot{j} = \dot{u} - \dot{T}s - T \dot{s}.$$ (16)

Inserting from (1) into (6) the inequality is obtained

$$\rho \dot{f} \leq -\rho \dot{T}s + (F_{c1} + J_1) \cdot \dot{a}_1 + (F_{c2} + J_2) \cdot \dot{a}_2 + T (\beta_3 J_1 + \beta_4 J_2) \cdot \nabla q + T [\nabla \odot (\beta_3 J_1) + \nabla \odot (\beta_4 J_2)] \cdot q.$$ (17)

From (16) follows

$$T \dot{s} = \dot{u} - \dot{T} s - \dot{j}.$$ (18)

Inserting from (1) into (18) and then into (7) the second law of thermodynamics $\alpha^s \geq 0$ has the form

$$\rho \dot{f} \leq -\rho s \dot{T} - T^{-1} \nabla T \cdot q + (F_{c1} + J_1) \cdot \dot{a}_1 + (F_{c2} + J_2) \cdot \dot{a}_2 + T [\nabla \odot (\beta_3 J_1 + \beta_4 J_2)] \cdot q + T (\beta_3 J_1 + \beta_4 J_2) \cdot \nabla q.$$ (19)

The following relation can be written for the rate of the free energy

$$\dot{j} = \frac{\partial f}{\partial T} \dot{T} + \frac{\partial f}{\partial q} \dot{q} + \frac{\partial f}{\partial a_1} \dot{a}_1 + \frac{\partial f}{\partial a_2} \dot{a}_2 + \frac{\partial f}{\partial J_1} \dot{J}_1 + \frac{\partial f}{\partial J_2} \dot{J}_2.$$ (20)

Further from (15) can be obtained

$$\dot{q} = T (\rho \alpha_{0})^{-1} [L_q q - \nabla (T)^{-1} - \nabla \odot (\beta_3 J_1 + \beta_4 J_2)],$$

$$\dot{J}_1 = T (\rho \alpha_{J_10})^{-1} [L_{J_1} J_1 - T^{-1} \dot{a}_1 - \beta_3 \nabla q],$$

$$\dot{J}_2 = T (\rho \alpha_{J_20})^{-1} [L_{J_2} J_2 - T^{-1} \dot{a}_2 - \beta_4 \nabla q].$$ (21)
Inserting from (20) and (21) into (19) the inequality has the form

\[- \rho \left( s + \frac{\partial f}{\partial T} \right) \dot{T} - \left[ \rho \frac{\partial f}{\partial \alpha_1} - \frac{\partial f}{\partial J_1} (\alpha_{J,0})^{-1} - (F_{c1} + J_1) \right] \cdot \dot{\alpha}_1 -
\]

\[- \left[ q + \frac{\partial f}{\partial q} (\alpha_{q,0})^{-1} \right] T^{-1} \cdot \nabla T +
\]

\[+ T \left\{ \beta_3 \left[ J_1 + \frac{\partial f}{\partial J_1} (\alpha_{J,0})^{-1} \right] + \beta_4 \left[ J_2 + \frac{\partial f}{\partial J_2} (\alpha_{J,0})^{-1} \right] \right\} \cdot \nabla q +
\]

\[+ T \left[ q + \frac{\partial f}{\partial q} (\alpha_{q,0})^{-1} \right] \cdot \left[ \nabla \circ (\beta_3 J_1 + \beta_4 J_2) \right] - T \left[ \frac{\partial f}{\partial q} (\alpha_{q,0})^{-1} L_q \right] \cdot q -
\]

\[- T \left[ \frac{\partial f}{\partial J_1} (\alpha_{J,0})^{-1} L_{J_1} \right] \cdot J_1 - T \left[ \frac{\partial f}{\partial J_2} (\alpha_{J,0})^{-1} L_{J_2} \right] \cdot J_2 \geq 0 .
\]

The inequality (22) is fulfilled for

\[s = - \frac{\partial f}{\partial T} , \quad (23)\]

\[\rho \frac{\partial f}{\partial \alpha_1} - \frac{\partial f}{\partial J_1} (\alpha_{J,0})^{-1} - (F_{c1} + J_1) = 0 \Rightarrow F_{c1} = \rho \frac{\partial f}{\partial \alpha_1} ; \quad J_1 = -(\alpha_{J,0})^{-1} \frac{\partial f}{\partial J_1} , \quad (24)\]

\[\rho \frac{\partial f}{\partial \alpha_2} - \frac{\partial f}{\partial J_2} (\alpha_{J,0})^{-1} - (F_{c2} + J_2) = 0 \Rightarrow F_{c2} = \rho \frac{\partial f}{\partial \alpha_2} ; \quad J_2 = -(\alpha_{J,0})^{-1} \frac{\partial f}{\partial J_2} , \quad (25)\]

\[\left( (\alpha_{q,0})^{-1} \frac{\partial f}{\partial q} + q \right) = 0 , \quad (26)\]

\[\beta_3 J_1 + \beta_4 J_2 + (\alpha_{J,0})^{-1} \beta_3 \frac{\partial f}{\partial J_1} + (\alpha_{J,0})^{-1} \beta_4 \frac{\partial f}{\partial J_2} = 0 , \quad (27)\]

\[\left( (\alpha_{q,0})^{-1} \frac{\partial f}{\partial q} \right) L_q = - \hat{\alpha} q , \quad (28)\]

\[\left( (\alpha_{J,0})^{-1} \frac{\partial f}{\partial J_1} \right) L_{J_1} = - \hat{\beta}_1 J_1 , \quad (29)\]

\[\left( (\alpha_{J,0})^{-1} \frac{\partial f}{\partial J_2} \right) L_{J_2} = - \hat{\beta}_2 J_2 , \quad (30)\]

where \( \hat{\alpha} \geq 0, \hat{\beta}_1 \geq 0, \hat{\beta}_2 \geq 0. \)

The conditions (26), (28), (29) and (30) are satisfied if the free energy is quadratic in \( q, J_1, J_2. \) From the evolution equations (15) or (21) follows

\[
\rho \frac{\partial f}{\partial a} = - \tau_q , \quad \frac{\rho}{T} \alpha_{J,0} L_{J_1}^{-1} = - \tau_{J_1} , \quad \frac{\rho}{T} \alpha_{J,0} L_{J_2}^{-1} = - \tau_{J_2} , \quad (31)
\]

where \( \tau_q, \tau_{J_1}, \tau_{J_2} \) are relaxation times. \( L_q, L_{J_1}, L_{J_2}, \) where \( L_{J_i}^{-1} = [(L_{J_i})_1^{-1}, (L_{J_i})_2^{-1}, \ldots], \) can be expressed if the evolution equations are written for the stationary and homogenous fluxes

\[L_q q = \nabla (T^{-1}) , \quad L_{J_1} J_1 = T^{-1} \dot{\alpha}_1 , \quad L_{J_2} J_2 = T^{-1} \dot{\alpha}_2 . \quad (32)\]

The first of these equations corresponds to Fourier’s law and therefore

\[L_q = (\lambda T^2)^{-1} . \quad (33)\]
Then from (31) follows

\[ L_q = \frac{\tau_q}{\lambda T^2}, \quad \alpha_{q0} = -\frac{\tau_q}{\rho \lambda T}. \quad (34) \]

\( L_{J_1}, L_{J_2} \) can be similarly obtained in the specific cases.

Let the given presumptions be summarized

1. (5) – the forms of the \( \alpha_s \),
2. (8) – the form of the entropy flux,
3. (14) – the form of the matrix \( L \) (a measure of the coupling state).

The origin of the above used forms 1., 2. is not often mentioned in literature. Further it is obvious that the basic assumptions are also the forms of the entropy and its flux. They are quadratic polynomials of the corresponding variables. All these assumptions allow very large amount of mathematical form variations.

3. EIT – multicomponent continuum

Let the multicomponent system consisting from chemical interacting components be taken into account. The other processes excluding the heat transfer are neglected for simplicity. The equation (1) has then the form

\[ \rho \dot{u} = -\nabla \cdot q. \quad (35) \]

The entropy \( s(u, q, c_k, J_k, Y_r) \) is the function of the internal energy, heat flux, concentration and the diffusion flux of the \( k \)-components and state of the \( r \)-chemical reactions. The entropy rate is written as follows

\[ s = \frac{\partial s}{\partial u} \dot{u} + \frac{\partial s}{\partial q} \cdot \dot{q} + \frac{\partial s}{\partial c_k} \dot{c}_k + \frac{\partial s}{\partial J_k} \cdot \dot{J}_k + \frac{\partial s}{\partial Y_r} \dot{Y}_r, \quad (36) \]

where

\[ \frac{\partial s}{\partial u} = \theta^{-1}, \quad \frac{\partial s}{\partial q} = \theta^{-1} \alpha_q(u, q, c_k, J_k, Y_r), \quad \frac{\partial s}{\partial c_k} = -\theta \rho^{-1} \mu_k, \]

\[ \frac{\partial s}{\partial J_k} = \theta^{-1} \alpha_{J_k}(u, q, c_k, J_k, Y_r), \quad \frac{\partial s}{\partial Y_r} = \theta^{-1} \alpha_{Y}^{(r)}(u, q, c_k, J_k, Y_r). \quad (37) \]

The similar presumptions according to the case (5) are

\[ \alpha_q = \alpha_{q0}(u) q, \quad \alpha_{J_k} = \alpha_{J_k0}(u) J_k, \quad \alpha_{Y}^{(r)} = \rho \alpha_{Y0}^{(r)} Y_r, \quad \theta = T. \quad (38) \]

That leads to

\[ \rho \dot{s} = -\nabla (T^{-1} q) + q \cdot \nabla T^{-1} + \rho T^{-1} \alpha_{q0} q \cdot \dot{q} - \]

\[ - (\rho T)^{-1} \mu_k \dot{c}_k + \rho T^{-1} \alpha_{J_k0} J_k \cdot \dot{J}_k + \rho T^{-1} \alpha_{Y0}^{(r)} Y_r \dot{Y}_r. \quad (39) \]

A further presumption deals with the entropy flux (like (8))

\[ J^s = T^{-1} q - T^{-1} \mu_k J_k, \quad (40) \]

where \( \mu_k \) is the chemical potential of the \( k \)-component. Inserting (39), (40) into (7) the entropy source is expressed

\[ \sigma^s = q \cdot (\nabla T^{-1} + T^{-1} \rho \alpha_{q0} \dot{q}) + J_k \cdot [T^{-1} \rho \alpha_{J_k0} \dot{J}_k - \nabla (T^{-1} \mu_k)] + \]

\[ + Y_r (T^{-1} \rho \alpha_{Y0}^{(r)} \dot{Y}_r) - T^{-1} \mu_k (\nabla \cdot J_k + \rho \dot{c}_k). \quad (41) \]
The terms in brackets are again the forces

\[
\begin{align*}
X_q &= \nabla T^{-1} + \rho T^{-1} \alpha q_0 \dot{q}, \\
X_{J_k} &= \rho T^{-1} \alpha_{J_k0} \dot{J}_k - \nabla (T^{-1} \mu_k), \\
X_Y &= \rho T^{-1} \alpha^{(r)}_{Y0} \dot{Y}_r, \\
X_{\mu} &= - (\nabla \cdot J_k + \rho \dot{c}_k).
\end{align*}
\]

The inequality (41) is fulfilled e.g. if

\[
[X_q, X_{J_k}, X_Y, X_{\mu}]^T = L [q, J_k, Y_r, \mu_k T^{-1}]^T,
\]

where the matrix of Onsager coefficients \( L \) satisfies the above mentioned conditions (13).

Let e.g.

\[
L = \begin{bmatrix}
L_q & 0 & 0 & 0 \\
0 & L_{J_k} & 0 & 0 \\
0 & 0 & L_Y & L_{Y\mu} \\
0 & 0 & L_{\mu Y} & L_{\mu}
\end{bmatrix}.
\]

The coupling between the mass and heat flux is omitted. The other non-zero matrix elements are the scalars according to Curie-Prigogine principle. Certain authors like e.g. [6] allow also the non-scalar coefficients to overcome Curie-Prigogine principle. Certain constrains valid for the matrix elements can be obtained if they are compared to the known constitutive equations.

Three last rows of (43) have the forms

\[
\begin{align*}
(a) \quad & \rho T^{-1} \alpha_{J_k0} \dot{J}_k - \nabla (T^{-1} \mu_k) = L_{J_k} J_k, \\
(b) \quad & \rho T^{-1} \alpha^{(r)}_{Y0} \dot{Y}_r = L_Y Y_r + L_{Y\mu} \mu_k T^{-1}, \\
(c) \quad & - (\nabla \cdot J_k + \rho \dot{c}_k) = L_{\mu Y} Y_r + L_{\mu} \mu_k T^{-1}.
\end{align*}
\]

From (45b, c) can be obtained

\[
- (\nabla \cdot J_k + \rho \dot{c}_k) = \frac{L_{\mu}}{L_{Y\mu}} \rho T^{-1} \alpha^{(r)}_{Y0} \dot{Y}_r + \left( L_{Y\mu} - \frac{L_Y L_{\mu}}{L_{Y\mu}} \right) Y_r.
\]

The term in brackets is the determinant of the matrix \( L \) last minor. If it is equal to zero then the usual equation (see [7] eq. (25)) for dissipation is obtained in the following form

\[
- (\nabla \cdot J_k + \rho \dot{c}_k) = \frac{L_{\mu}}{L_{Y\mu}} \rho T^{-1} \alpha^{(r)}_{Y0} \dot{Y}_r.
\]

From (45a) the evolution equation of the dissipation flux is expressed

\[
\frac{\rho T^{-1} \alpha_{J_k0}}{L_{J_k}} J_k - J_k = \frac{1}{L_{J_k}} \nabla (T^{-1} \mu_k),
\]

where

\[
\frac{\rho T^{-1} \alpha_{J_k0}}{L_{J_k}} = \tau J_k,
\]
is the corresponding relaxation time. It corresponds to ([2] eq. (10.7)) if the coupling between mass fluxes and the chemical potentials is neglected. The equation (45b) defines the velocity of the $r$-chemical reaction.

Let the given presumptions be again summarized

1. (38) – form of the $\alpha_s$,
2. (40) – form of the entropy flux,
3. (44) – form of the $L$ – matrix (measure of the coupling state).

It is again obvious that the basic assumptions are also the forms of the entropy and its flux. They are quadratic polynomials of the corresponding variables with certain linear terms $(u, c_k)$. Similar approach can be found in [6] where the quadratic polynomial for the free energy is chosen. A lot of freedom remains in the concrete choice. If (41) is compared with the equation (23) in [7] the necessity to choose the linear entropy dependence on the state of the chemical reaction $Y_r$ is obvious. Then the term $\rho T^{-1}A^{(r)}_Y$ equals to $A_rT^{-1}$ where $A_r$ is the affinity of the $r$-reaction.

Inserting from (35) and (39) into (16) the free energy is given

$$\dot{f} = -\dot{T}s - \alpha_{q0} \mathbf{q} \cdot \dot{\mathbf{q}} + \mu_k \dot{c}_k - \alpha_{J_k0} \mathbf{J}_k \cdot \dot{\mathbf{J}}_k - \alpha^{(r)}_Y Y_r \dot{Y}_r.$$  

Inserting form (35) and (40) in (18) and then into (7) the new form of the 2nd law of thermodynamics can be written

$$\rho \dot{f} \leq -\rho \dot{T}s - T^{-1}\nabla T \cdot \mathbf{q} + T^{-1}\nabla T \cdot (\mu_k \mathbf{J}_k) - \nabla \cdot (\mu_k \mathbf{J}_k).$$  

Let the rate of the free energy $f(t, \mathbf{q}, c_k, \mathbf{J}_k, Y_r)$ be

$$\dot{f} = \frac{\partial f}{\partial T} \dot{T} + \frac{\partial f}{\partial \mathbf{q}} \cdot \dot{\mathbf{q}} + \frac{\partial f}{\partial c_k} \dot{c}_k + \frac{\partial f}{\partial \mathbf{J}_k} \cdot \dot{\mathbf{J}}_k + \frac{\partial f}{\partial Y_r} \dot{Y}_r.$$  

From the first row of the matrix equation (43) follows

$$\dot{\mathbf{q}} = \frac{1}{\tau_q} \left( \mathbf{q} - \frac{1}{L_q} \nabla T^{-1} \right), \quad \tau_q = \frac{\rho T^{-1} \alpha_{q0}}{L_q},$$

where $\tau_q$ is the relaxation time. From the remaining rows of (43) or from (45a, b, c) the following relations arise

$$\dot{\mathbf{J}}_k = \frac{1}{\tau_{J_k}} \left[ \mathbf{J}_k + \frac{1}{L_{J_k}} \nabla (T^{-1} \mu_k) \right], \quad \tau_{J_k} = \frac{\rho T^{-1} \alpha_{J_k0}}{L_{J_k}},$$

$$\dot{Y}_r = \frac{1}{\tau_Y} \left( Y_r + \frac{L_{Y_k}}{L_Y} \mu_k T^{-1} \right), \quad \tau_Y = \frac{\rho T^{-1} \alpha^{(r)}_Y}{L_Y},$$

$$\dot{c}_k = -\rho^{-1} \nabla \cdot \mathbf{J}_k - \rho^{-1} \mu_k Y_r - \rho^{-1} \mu_k T^{-1}.$$  

Let insert from (52), (53) and (54) into the inequality (51)

$$-\dot{T} \rho \left( s + \frac{\partial f}{\partial T} \right) - \frac{\nabla T}{T} \cdot \left( \mathbf{q} - \mu_k \mathbf{J}_k - \rho \frac{1}{T} L_{J_k} T \frac{\partial f}{\partial \mathbf{q}} - \rho \frac{\mu_k}{L_{J_k} T \tau_{J_k}} \frac{\partial f}{\partial \mathbf{J}_k} \right) -$$

$$- \nabla \cdot \mathbf{J}_k \left( -\frac{\partial f}{\partial c_k} + \mu_k \right) - \nabla \mu_k \cdot (\mathbf{J}_k + \rho \frac{1}{T} L_{J_k} \tau_{J_k} \frac{\partial f}{\partial \mathbf{J}_k} - \rho \frac{\mathbf{q}}{\tau_q} \frac{\partial f}{\partial \mathbf{q}} +$$

$$+ Y_r \left( \mu_k \frac{\partial f}{\partial c_k} + \rho \frac{1}{T} \frac{\partial f}{\partial Y_r} \right) + \frac{\mu_k}{T} \left( -\rho \frac{L_{Y_k}}{L_Y} \frac{\partial f}{\partial Y_r} + \mu_k \frac{\partial f}{\partial c_k} \right) -$$

$$- \rho \frac{\mathbf{J}_k}{\tau_{J_k}} \frac{\partial f}{\partial \mathbf{J}_k} \geq 0.$$
The inequality (55) is fulfilled if the following equations hold

\[ -\frac{\partial f}{\partial T} = s , \]  
\[ \mu_k = \frac{\partial f}{\partial c_k} , \]  
\[ J_k = -\rho \frac{1}{T L_{J_k} \tau_{J_k}} \frac{\partial f}{\partial J_k} , \]  
\[ \rho \frac{1}{T L \tau_q} \frac{\partial f}{\partial q} = \rho \frac{\mu}{T L_{J_k} \tau_{J_k}} \frac{\partial f}{\partial J_k} + q - \mu_k J_k = 0 , \]  
\[ \rho \frac{1}{\tau_q} \frac{\partial f}{\partial q} = -\delta_q q , \]  
\[ L_{\mu_Y} \frac{\partial f}{\partial c_k} - \rho \frac{1}{\tau_Y} \frac{\partial f}{\partial Y_r} = \delta_Y^{(r)} Y_r , \]  
\[ L_{\mu} \frac{\partial f}{\partial c_k} - \rho \frac{L_{Y_r}}{\tau_Y \tau_{Y_r}} \frac{\partial f}{\partial Y_r} = \delta_{\mu} \mu_k , \]  
\[ -\rho \frac{1}{\tau_{J_k}} \frac{\partial f}{\partial J_k} = \hat{\delta}_{J_k} J_k , \]

where \( \delta_q \) are non-negative.

4. Integration of EIT and IVT

The integration of both theories IVT and EIT seems to be logic for the processes with different relaxation times. Comparing the equations of the entropy production (9) and (41) the following relation can be written

\[ \sigma^* = q \cdot \left[ \nabla T^{-1} + \rho T^{-1} \alpha_{q0} \hat{q} + \nabla \cdot (\beta_3 J_1) + \nabla \cdot (\beta_4 J_2) \right] + \]  
\[ + J_1 \cdot (T^{-1} \hat{a}_1 + \rho T^{-1} \alpha_{J_1} \hat{J}_1 + \beta_3 \nabla q) + \]  
\[ + J_2 \cdot (T^{-1} \hat{a}_2 + \rho T^{-1} \alpha_{J_2} \hat{J}_2 + \beta_4 \nabla q) + \]  
\[ + J_k \cdot (\rho T^{-1} \alpha_{J_k} \hat{J}_k - \nabla (T^{-1} \mu_k)) + \]  
\[ + T^{-1} (F_{c1} - F_{e1}) \cdot \hat{a}_1 + T^{-1} (F_{c2} - F_{e2}) \cdot \hat{a}_2 + \rho T^{-1} A \cdot \hat{\xi} \geq 0 . \]  

If \( \alpha_{J_1} = 0 \), \( \rho Y_r \alpha_{Y_r} = a_{\text{chem}} \), \( \rho \hat{c}_k = -\nabla \cdot J_k \), etc. then (64) corresponds to the IVT results – compare it with [7]. If the fluxes \( J_{1,2} \) do not appear in the relation \( \dot{u} \) (the balance equation) and if \( \beta_{3,4} = 0 \) then the fluxes \( J_{1,2} \) can be mentioned in the theory as the internal variables. From the mentioned point of view EIT seems to be much more general than IVT.

If the free energy using (17), (19), (51)–(54) is introduced then

\[ \dot{f} = -\dot{T} s - \alpha_{q0} q \cdot \dot{q} + \rho^{-1} (F_{c1} \cdot \dot{a}_1 + F_{c2} \cdot \dot{a}_2) - \alpha_{J_1} \hat{J}_1 - \alpha_{J_2} \hat{J}_2 + \]  
\[ + \mu_k \hat{c}_k - \alpha_{J_k} \hat{J}_k - \alpha_{Y_r} Y_r \hat{Y}_r - A \cdot \hat{\xi} , \]  
\[ \rho \dot{f} \leq -\rho s \dot{T} - T^{-1} \nabla T \cdot q + (F_{c1} + \hat{J}_1) \cdot \hat{a}_1 + (F_{c2} + \hat{J}_2) \cdot \hat{a}_2 + T [\nabla \cdot (\beta_3 J_1 + \]  
\[ + \beta_4 J_2)] + T \cdot (\beta_3 J_1 + \beta_4 J_2) \cdot \nabla q + T^{-1} \nabla T \cdot (\mu_k \hat{J}_k - \nabla (\mu_k \hat{J}_k)) . \]
Let the forces and the corresponding fluxes be summarized

\[
\begin{align*}
X_q &= \nabla T^{-1} + \rho T^{-1} \alpha_{q0} \dot{q} + \nabla \cdot (\beta_3 J_1) + \nabla \cdot (\beta_4 J_2), \\
X_{J_1} &= T^{-1} \dot{a}_1 + \rho T^{-1} \alpha_{J_10} \dot{J}_1 + \beta_3 \nabla q, \\
X_{J_2} &= T^{-1} \dot{a}_2 + \rho T^{-1} \alpha_{J_20} \dot{J}_2 + \beta_4 \nabla q, \\
X_{a_1} &= T^{-1} \dot{a}_1, \\
X_{a_2} &= T^{-1} \dot{a}_2, \\
X_{J_k} &= \rho T^{-1} \alpha_{J_k} \dot{J}_k - \nabla (T^{-1} \mu_k), \\
X_\mu &= -\nabla \cdot J_k - \rho \dot{c}_k, \\
X_\xi &= \rho T^{-1} \dot{\xi}.
\end{align*}
\]

The inequality (64) is satisfied if e.g.

\[
[X_q, X_{J_1}, X_{J_2}, X_{a_1}, X_{a_2}, X_{J_k}, X_\mu, X_\xi]^T = \begin{bmatrix}
L_q & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & L_{J_1} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & L_{J_2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & L_{a_1} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & L_{a_2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & L_{J_k} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & L_\mu & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & L_\mu \end{bmatrix}^T, 
\]

As an example, the mostly uncoupled case is shown when the matrix of Onsager coefficients is diagonal with an exception of \(L_{Y\mu}, L_{\mu Y}\)

\[
L = \begin{bmatrix}
L_q & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & L_{J_1} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & L_{J_2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & L_{a_1} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & L_{a_2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & L_{J_k} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & L_\mu & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & L_\mu \end{bmatrix}. 
\]

The evolution equations are then

\[
\begin{align*}
\dot{q} &= \frac{T}{\rho \alpha_{q0}} \left[ L_q q - \nabla T^{-1} - \nabla \cdot (\beta_3 J_1 + \beta_4 J_2) \right], \\
\dot{a}_i &= T L_{a_i} F_{\text{dis} i}, \quad i = 1, 2, \\
\dot{J}_1 &= \frac{T}{\rho \alpha_{J_10}} (L_{J_1} J_1 - L_{a_1} F_{\text{dis} 1} - \beta_3 \nabla q), \\
\dot{J}_2 &= \frac{T}{\rho \alpha_{J_20}} (L_{J_2} J_2 - L_{a_2} F_{\text{dis} 2} - \beta_4 \nabla q), \\
\dot{J}_k &= \frac{T}{\rho \alpha_{J_k0}} \left[ L_{J_k} J_k + \nabla (T^{-1} \mu_k) \right], \\
\dot{Y}_r &= \frac{T}{\rho \alpha_{Y0}} \left( L_Y Y_r + L_{\mu Y} \frac{\mu_k}{T} \right), \\
\dot{c}_k &= -\rho^{-1} \left( L_{\mu} \frac{\mu_k}{T} + L_{\mu Y} Y_r + \nabla \cdot J_k \right), \\
\dot{\xi} &= \frac{T}{\rho} L_A A.
\end{align*}
\]
Inserting from (70) into (65) and (66) and taking into account the rate of the free energy $f(T, q, a_1, a_2, J_1, J_2, c_k, J_k, Y_r, \xi)$

\[
\dot{j} = \frac{\partial f}{\partial T} \dot{T} + \frac{\partial f}{\partial q} \cdot \dot{q} + \frac{\partial f}{\partial a_1} \cdot \dot{a}_1 + \frac{\partial f}{\partial a_2} \cdot \dot{a}_2 + \frac{\partial f}{\partial J_1} \cdot \dot{J}_1 + \\
+ \frac{\partial f}{\partial J_2} \cdot \dot{J}_2 + \frac{\partial f}{\partial c_k} \cdot \dot{c}_k + \frac{\partial f}{\partial J_k} \cdot \dot{J}_k + \frac{\partial f}{\partial Y_r} \cdot \dot{Y}_r + \frac{\partial f}{\partial \xi} \cdot \dot{\xi},
\]

from (66), (70) and (71) the following relation is obtained

\[
0 \leq -\rho \left( s + \frac{\partial f}{\partial T} \right) \dot{T} - \left[ \rho \frac{\partial f}{\partial a_1} - \frac{\partial f}{\partial J_1} \alpha_{J_1}^{-1} - (F_{c1} + J_1) \right] \cdot \dot{a}_1 - \\
- \left[ \rho \frac{\partial f}{\partial a_2} - \frac{\partial f}{\partial J_2} \alpha_{J_2}^{-1} - (F_{c2} + J_2) \right] \cdot \dot{a}_2 - \\
- \left( \rho \frac{\partial f}{\partial q} \frac{1}{\tau_q TL_q} + \rho \frac{\partial f}{\partial J_k} \frac{\mu_k}{\tau_k TL_k} + q - \mu_k J_k \right) \cdot \nabla T - \\
+ T \left( \frac{\partial f}{\partial J_1} \beta_3 \alpha_{J_1}^{-1} + \frac{\partial f}{\partial J_2} \beta_4 \alpha_{J_2}^{-1} + \beta_3 J_1 + \beta_4 J_2 \right) \cdot \nabla q + \\
+ T \left( \frac{\partial f}{\partial q} \alpha^{-1} q_0 + q \right) \cdot \nabla (\beta_3 J_1) + T \left( \frac{\partial f}{\partial q} \alpha^{-1} q_0 + q \right) \cdot \nabla (\beta_4 J_2) - \\
- T \frac{\partial f}{\partial q} \frac{L_q}{\alpha_{q0}} \cdot \dot{q} - T \frac{\partial f}{\partial J_1} \frac{L_{J_1}}{\alpha_{J_10}} \cdot \dot{J}_1 - T \frac{\partial f}{\partial J_2} \frac{L_{J_2}}{\alpha_{J_20}} \cdot \dot{J}_2 - \\
- \left( \mu_k - \frac{\partial f}{\partial c_k} \right) \nabla \cdot \dot{J}_k - \left( J_k + \rho \frac{\partial f}{\partial J_k} \frac{1}{\tau_k TL_k} \right) \cdot \nabla \mu_k + \\
+ \left( \frac{\partial f}{\partial c_k} L_{\mu Y} - \frac{\partial f}{\partial Y_r} \frac{1}{\tau_Y} \right) Y_r + \left( \frac{\partial f}{\partial c_k} L_{\mu Y} - \frac{\partial f}{\partial Y_r} \frac{1}{\tau_Y} \frac{L_{Y\mu}}{\tau_Y} \right) \mu_k - \\
- \left( \rho \frac{\partial f}{\partial J_k} \frac{1}{\tau_k TL_k} \right) \cdot \dot{J}_k - \frac{\partial f}{\partial \xi} TL_A \cdot A,
\]

where the relaxation times are given by (53), (54).

From (72) follows

\[
- \frac{\partial f}{\partial T} = s, \quad \frac{\partial f}{\partial q} = -\alpha_{q0} q, \quad \frac{\partial f}{\partial a_1} = -\rho^{-1} F_{c1}, \quad \frac{\partial f}{\partial a_2} = -\rho^{-1} F_{c2}, \\
\frac{\partial f}{\partial J_1} = -\alpha_{J_1} J_1, \quad \frac{\partial f}{\partial J_2} = -\alpha_{J_2} J_2, \quad \frac{\partial f}{\partial Y_r} = -\alpha_{Y_0} Y_r, \quad \mu_k = \frac{\partial f}{\partial c_k},
\]

\[
J_k = -\rho \frac{\partial f}{\partial J_k} \frac{1}{\tau_k TL_k}, \quad \frac{\partial f}{\partial \xi} = -A.
\]

The brackets need to be equal to zero or the terms should be positive in the first nine and the last two terms in (72). It is fulfilled for (73)! The following positive conditions can be written for the remaining terms (72)

\[
\frac{\partial f}{\partial c_k} L_{\mu Y} - \rho \frac{\partial f}{\partial Y_r} \frac{1}{\tau_Y} = \delta^{(r)} Y_r, \quad \frac{\partial f}{\partial c_k} L_{\mu Y} - \rho \frac{\partial f}{\partial Y_r} \frac{L_{Y\mu}}{\tau_Y} = \delta_{\mu} \mu_k,
\]

where both $\delta_s$ are non-negative.
5. Example

The case published in [2] is chosen as an example of the above mentioned formalism usage. Let \( a_1 \sim \{ e, \tilde{e} \}, a_2 \sim 0, F_{c1} \sim \{ s', \tilde{\tau}' \}, F_{e1} = F_{c1}, J_1 \sim \{ s'', \tilde{\tau}'' \}, F_{e2} = F_{c2}, J_2 = 0 \), where \( e = \varepsilon_i^1 \) and \( s', s'' \) is elastic and viscous hydrostatic stress, respectively. \( \tilde{e}, \tilde{\tau}', \tilde{\tau}'' \) is the deviator of the deformation tensor, the deviator of the elastic and viscous stress, respectively. It gives

\[
\tau = \tau' + \tau'', \quad \tau' = s' I + \tilde{\tau}', \quad \tau'' = s'' I + \tilde{\tau}'', \quad \varepsilon = e I + \tilde{\varepsilon}. \tag{75}
\]

Inserting (75) into (1) and (6) follows

\[
\rho \dot{u} = F_{c1} \cdot \dot{\mathbf{a}}_1 + J_1 \cdot \dot{\mathbf{a}}_1 = s' \dot{e} + \tilde{\tau}' \cdot \dot{\tilde{e}} + s'' \dot{\tilde{e}} + \tilde{\tau}'' \cdot \ddot{\tilde{e}}, \tag{76}
\]

\[
\rho \dot{s} = T^{-1}(F_{c1} - F_{e1} + J_1) \cdot \dot{\mathbf{a}}_1 + \rho T^{-1} \alpha_{J,0} \mathbf{J}_1 \cdot \dot{\mathbf{J}}_1 = T^{-1}(s'' \dot{e} T^{-1} + \tilde{\tau}'' \cdot \dot{\tilde{e}}) + \rho T^{-1}(\alpha_{J,01} s'' s'' + \alpha_{J,02} \tilde{\tau}'' \cdot \ddot{\tilde{\tau}}''), \tag{77}
\]

where \( \alpha_{J,0} = (\alpha_{J,01}, \alpha_{J,02}) \). Then from (10) follows

\[
X_{J_1} = (T^{-1} \dot{e} + \rho T^{-1} \alpha_{J,01} s'', T^{-1} \dot{\tilde{e}} + \rho T^{-1} \alpha_{J,02} \dot{\tilde{\tau}}''). \tag{78}
\]

Let \( L_{J_1} = (L_{J,11}, L_{J,12}) \). Then from the second equation in (15) follows

\[
T^{-1} \dot{e} + \rho T^{-1} \alpha_{J,01} s'' = L_{J,11} s'', \quad T^{-1} \dot{\tilde{e}} + \rho T^{-1} \alpha_{J,02} \dot{\tilde{\tau}}'' = L_{J,12} \tilde{\tau}'' . \tag{79}
\]

These equations can be transferred into the following form

\[
\tau_s s'' + s'' = \frac{1}{T L_{J,11}} \dot{\tilde{e}}, \quad \tau_s \dot{\tilde{\tau}}'' + \tilde{\tau}'' = \frac{1}{T L_{J,12}} \ddot{\tilde{\tau}}, \tag{80}
\]

where for \( \alpha_{J,01} < 0, \alpha_{J,02} < 0 \)

\[
\tau_s = -\frac{\rho \alpha_{J,01}}{T L_{J,11}}, \quad \tau_{\tilde{\tau}} = -\frac{\rho \alpha_{J,02}}{T L_{J,12}}. \tag{81}
\]

Let \( \tilde{\tau}'', s'' \) be exchanged by \( \tilde{\tau}, s \) using (76) and Hook’s law in the forms \( e = s’/(3 \lambda + 2 \mu), \tilde{e} = \tilde{\tau}'/(2 \mu) \). Finally the constitutive equations for the Poynting-Thompson body are

\[
\tau_s \dot{s} + s = 3 K (e + \tau_s' \dot{e}), \quad \tau_s' = \frac{1}{T L_{J,11}} + \tau_s, \tag{82}
\]

\[
\tau_{\tilde{\tau}} \dot{\tilde{\tau}} + \tilde{\tau} = 2 G (\tilde{e} + \tau_{\tilde{\tau}}' \dot{\tilde{e}}), \quad \tau_{\tilde{\tau}}' = \frac{1}{T L_{J,12}} + \tau_{\tilde{\tau}},
\]

where \( 3 \lambda + 2 \mu = 3 K \) and \( 2 \mu = 2 G \). For \( \tau_{\tilde{\tau}} = 0 \) the Kelvin-Voigt continuum and for \( G = 0 \) the Maxwell continuum is obtained.

COMMENT: The Poynting-Thompson continuum corresponds in the 1D case with the four element body consisting from one spring and the Maxwell continuum in series.
6. Conclusion

The main results for EIT were summarized and the main assumptions considered in the theory were pointed out. The general integration formulation using both EIT and IVT were shown in the last part of the paper. It will be used in the future modelling of the living tissues – above all the smooth muscles – where the chemical and diffusion processes are crucial and should be taken into account.

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Literatura


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