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## Toward the thermodynamic modeling of reacting ionic mixtures

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**Abstract** Based on the Müller–Liu entropy principle and the axioms of constitutive theory, a continuum model for reacting ionic mixtures is presented. The influence of microscopic structure on the mixture dynamics is taken into account through the thermodynamics of polar materials. Moreover, mechanical balance laws for classical mixtures under influence of electromagnetic fields and quasi-electrostatic Maxwell's equations are briefly shown. With an appropriate constitutive model for a diluted and isotropic mixture of non-volatile solutes and by considering the same temperature field for all constituents, constraints on constitutive quantities are imposed, and the conditions for the thermodynamic equilibrium are established from the entropy principle. Furthermore, the nonlinear nature of chemical reactions as well as the reciprocal nature of some irreversible processes is highlighted. Unlike the classical approach for electrolyte solutions, the current constitutive model incorporates thermoelectric and electro-kinetic phenomena into the phenomenological equations, providing a more comprehensive approach of electrolyte solutions dynamics.

**Keywords** Electrolyte solutions · Entropy principle · Constitutive equations · Chemical reactions

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## 1 Introduction

The study of dynamic properties of reacting ionic mixtures, also called of electrolyte solutions, has occupied a central position in physical chemistry since the beginning of twentieth century. The development of many experimental and theoretical works about electrolytic dissociation, ionic migration, and conductance made possible to clarify the electrical nature of matter and the role of ion–ion and ion–solvent interactions in the properties of electrolyte solutions, particularly the aqueous ones.

Most of the theoretical models developed for electrolyte solutions by now have been based on statistical mechanics approaches whose focuses rely on the time-averaged spatial distribution of ions [2,16]. According to these models, a volume element of the solution is completely filled with a dielectric continuum in which discrete point charges, regarded as hard spheres, are immersed. Evidently, these approximations are shortcoming because real ions are not hard spheres, neither the solvent is a dielectric continuum. However, in the limit of very diluted solutions, these approaches are acceptable as Debye and Hückel demonstrated in [6].

In the Debye–Hückel model, thermodynamic properties of the solution are calculated from the electrostatic interaction energy between an ion, chosen as a reference, and all other ions in solution. In order to determinate the interaction energy, one considers that the averaged distribution of ions around the reference one follows the Boltzmann distribution law. Moreover, the relation between the charge density of each ion and the electrostatic potential can be given by the Poisson’s equation. The combination of these two equations leads to the so-called Poisson–Boltzmann equation, which, in general, is solved by numerical or series methods. However, to make further progress, Debye and Hückel focused on systems where the average electrostatic potential is much smaller than the thermal energy. This is a sufficient condition to linearize the Poisson–Boltzmann equation and solve it analytically. Then, using the linearized form of the Poisson–Boltzmann equation, the Debye–Hückel model provides theoretical results that are in good agreement with experimental data for very diluted solutions only.

In view of the limitations of the Debye–Hückel model, other theoretical models based on more realistic assumptions have been developed. Many of these models are founded on the use of the unlinearized Poisson–Boltzmann equation, the virial expansion of the excess Gibbs energy (Pitzer equation) [32,33], and the intermolecular potential theory (McMillan–Mayer theory) [25]. Nevertheless, despite the impressive success reached by these models, the lack of data about ionic and molecular *radii*, dielectric saturation, and electrostriction effects has hindered the application of them in more complex systems. Even with the advances in computational molecular dynamics, the determination of thermodynamic properties of electrolyte solutions is frequently a long and tedious process as it requires several computer cycles *per* chemical species. As a result, continuum models for mixtures have become an alternative approach, especially with the progresses obtained in electrorheological fluids and continuum mixtures models along the last decades. For instance, Maugin and co-authors [8,27,28] developed various continuum models to study the behavior of polyelectrolytes in non-homogeneous velocity gradient flows, either in the presence of electric fields or not. Furthermore, several continuum models [18,40] have been recently proposed in order to associate the material properties of electrorheological fluids to measurable macroscopic quantities.

The literature provides numerous works about constitutive modeling of polyelectrolytes, ionic polymer–metal composites, and electrorheological fluids with practical applications in automotive industries, polishing solutions, biomedical devices, *etc.* In [34,52], phenomenological models of ions transport were given with basis in the linear irreversible thermodynamics. In [31], Placidi and co-authors provided a continuum model for polymer–metal composites, where chemically induced deformations are described through a distortion field induced by solvated ions. However, although several continuum models are available for electrolyte mixtures, the most fundamental aspects of electrolyte dynamics have not been sufficiently explored yet. Hence, the aim of this work is to propose a general thermoelectrochemical theory to investigate the diffusive, reactive, and advective structures of diluted electrolyte solutions of non-volatile solutes. These solutions present close connection with the fields of Biochemistry (blood is an ion carrier and changes in the ions concentrations affect the blood flow) and Geology (soils with high concentration of ions flow faster), and differ from the polyelectrolyte ones because they do not contain ionic or polarizable macromolecules, but only monoatomic or molecular ions of low molecular weight.

In Sect. 2, the kinematics and the dynamics of reacting ionic mixtures are outlined by emphasizing the microscopic structure of the mixture. In turn, in Sect. 3, the entropy inequality is formulated and the use of the Müller–Liu entropy principle is advocated. Furthermore, thermodynamic restrictions on constitutive functions and their consequences for diluted electrolyte solutions whose constituents have the same temperature field are presented. In order to assess the implications of this constitutive theory for electrolyte

solutions, some results are compared with those of classical thermostatics. Finally, Sect. 4 summarizes the work.

In the present investigation, the continuum mixture obeys the postulates of the classical theory of mixtures proposed by Truesdell [41] and all fields are given in the Eulerian description. For convenience, only Cartesian tensors are employed, and all equations are invariant under Galilean transformations, including the Maxwell's equations. This implies that Maxwell's equations are used conforming the quasi-electrostatic approximation [26]. Moreover, the electrodynamics of the mixture is in accord with the Chu formulation of moving media [15].

## 2 Kinematics and balance laws

Let  $\mathcal{B}$  be a mixture of  $n$  constituents  $\mathcal{B}_a$ , such that a particle of  $\mathcal{B}_a$  is represented by  $X_a$  with  $a = 1, \dots, n$ , being the index  $n$  reserved for the solvent. Moreover, let a region of the Euclidean space  $\mathcal{E}$  in the current configuration be simultaneously occupied by different constituent particles. Thus, if  $\mathbf{X}_a$  is the material coordinate in some reference configuration  $\kappa$ , the motion  $\mathbf{x} = \mathbf{x}_a(\mathbf{X}_a, t)$  of a constituent  $a$  is a smooth function of space and time, which relates a particle  $X_a$  to a place  $\mathbf{X}_a$  at the time  $t$  in the reference configuration  $\kappa$ .

Each constituent has its own kinematics. The velocity and acceleration of a constituent  $a$  at the time  $t$  are, respectively,

$$\mathbf{v}_a \equiv \frac{\partial \mathbf{x}_a(\mathbf{X}_a, t)}{\partial t}, \quad \mathbf{a}_a \equiv \frac{\partial^2 \mathbf{x}_a(\mathbf{X}_a, t)}{\partial t^2}. \quad (2.1)$$

Likewise, each  $\mathcal{B}_a$  has its own mass and, consequently, its positive mass density  $\rho_a(\mathbf{x}, t)$ , at each point  $\mathbf{x}$  and time  $t$ . The mass density of the whole mixture,  $\rho(\mathbf{x}, t)$ , is related to  $\rho_a(\mathbf{x}, t)$  by

$$\rho \equiv \sum_{a=1}^n \rho_a. \quad (2.2)$$

At every  $(\mathbf{x}, t)$ , one also defines the mass concentration of  $\mathcal{B}_a$  as

$$\xi_a \equiv \frac{\rho_a}{\rho}, \quad (2.3)$$

whence Eqs. (2.2) and (2.3) imply  $\sum_{a=1}^n \xi_a = 1$ .

The mean velocity of  $\mathcal{B}$ ,  $\mathbf{v}(\mathbf{x}, t)$ , is defined by

$$\rho \mathbf{v} \equiv \sum_{a=1}^n \rho_a \mathbf{v}_a, \quad (2.4)$$

and the translational diffusion velocity of  $\mathcal{B}_a$  is

$$\mathbf{u}_a = \mathbf{v}_a - \mathbf{v}. \quad (2.5)$$

Then, it follows from Eqs. (2.2), (2.4) and (2.5) that  $\sum_{a=1}^n \rho_a \mathbf{u}_a = \mathbf{0}$ .

Until now, the kinematics of reacting ionic mixtures obeys the general framework of classical mixtures set up by Truesdell [41]. However, in contrast to the classical theories of mixtures, it has long been accepted that the dynamics of electrolyte solutions depends on the short-range and long-range interactions among the constituent particles. Following Eringen and Toupin's ideas [7, 9, 20, 43, 44], the interactions among the constituent particles are accounted for by considering the electrolyte solution as a polar elastic dielectric medium. Then, under an applied electric field, which may be due to an external source and/or generated by dissociated ions in solution, constituent particles will interact with the electric field, producing extrinsic body couples and extrinsic surface couples. Consequently, to describe accurately the material behavior of such solutions, it is necessary to use the theoretical framework of polar theories, where the action of extrinsic body couples and surface body couples caused by electromagnetic fields on the constituent particles are properly considered.

Polar theories differently from non-polar ones encompass not only the short-range interactions as the classical local theories, but also the long-range forces [42]. In this sense, electrolyte solutions differ from the classical mixtures because the behavior of their material points is influenced by all points of the solution independently of the ions concentrations. Thus, in order to include the microscopic structure of electrolyte

solutions into the continuum model, new kinematic variables are associated with each point  $(\mathbf{x}, t)$  of the mixture. Specifically, in contrast to classical continuum mechanics, where the only kinematic vector field is the velocity  $\mathbf{v}(\mathbf{x}, t)$ , polar materials present two independent kinematic vector fields to describe the translational and rotational motion of the fluid particles. If the mechanics of rigid bodies is assumed, each constituent particle possesses a spin field  $\mathbf{s}_a(\mathbf{x}, t)$  and a local angular velocity  $\boldsymbol{\omega}_a(\mathbf{x}, t)$  which are interrelated by

$$\mathbf{s}_a \equiv \mathbf{I}_a \boldsymbol{\omega}_a, \quad (2.6)$$

where  $\mathbf{I}_a$  is the inertia momentum tensor. Moreover, in structured media, the local angular velocity of the particle does not coincide with the angular velocity of the mixture, *viz.*, vorticity  $\mathbf{w}(\mathbf{x}, t)$ . Then, the local angular velocity of a constituent particle in relation to the fluid vorticity is

$$\boldsymbol{\varpi}_a \equiv \boldsymbol{\omega}_a - \mathbf{w}. \quad (2.7)$$

Clearly, all definitions can be extended to the mixture, so one may equally assign to the mixture particles a spin field  $\mathbf{s}(\mathbf{x}, t)$ , a local angular velocity  $\boldsymbol{\omega}(\mathbf{x}, t)$ , and an inertia tensor  $\mathbf{I}(\mathbf{x}, t)$  which are, respectively, related to those of the constituents by

$$\rho \mathbf{s} \equiv \sum_{a=1}^n \rho_a \mathbf{s}_a, \quad \rho \boldsymbol{\omega} \equiv \sum_{a=1}^n \rho_a \boldsymbol{\omega}_a, \quad \rho \mathbf{I} \equiv \sum_{a=1}^n \rho_a \mathbf{I}_a. \quad (2.8)$$

Similarly to the translational motion, one defines the rotational diffusion velocity of a constituent  $a$  at  $(\mathbf{x}, t)$  as

$$\mathbf{v}_a \equiv \boldsymbol{\omega}_a - \boldsymbol{\omega}, \quad (2.9)$$

such that  $\sum_{a=1}^n \rho_a \mathbf{v}_a = \mathbf{0}$ .

Balance equations of mass, linear momentum, spin, and energy of a reacting ionic mixture were derived by Reis and Bassi in [35], where they were comprehensively discussed. However, for the sake of convenience, the balance equations are outlined below.

Each constituent is regarded locally as an open system, so balance laws are postulated individually for each constituent of the mixture. The material behavior of constituents of a reacting ionic mixture is governed by:

*Balance of mass*

$$\frac{d^a \rho_a}{dt} + \rho_a \operatorname{div}(\mathbf{v}_a) - c_a = 0, \quad (2.10)$$

*Balance of linear momentum*

$$\rho_a \frac{d^a \mathbf{v}_a}{dt} - \operatorname{div}(\mathbf{T}_a) - \rho_a \mathbf{b}_a - q_a \mathbf{E}_a - \mathbf{P}_a \cdot \nabla \mathbf{E}_a - \mathbf{m}_a = 0, \quad (2.11)$$

*Balance of spin*

$$\rho_a \mathbf{I}_a \frac{d^a \boldsymbol{\omega}_a}{dt} - \operatorname{div}(\mathbf{C}_a) + 2\hat{\mathbf{t}}_a - \mathbf{P}_a \times \mathbf{E}_a - \rho_a \mathbf{l}_a - \boldsymbol{\tau}_a = 0, \quad (2.12)$$

*Balance of energy*

$$\rho_a \frac{d^a \varepsilon_a}{dt} + \operatorname{div}(\mathbf{h}_a) - \mathbf{T}_a \cdot \nabla \mathbf{v}_a - \mathbf{C}_a \cdot \nabla \boldsymbol{\omega}_a - 2\boldsymbol{\omega}_a \cdot \hat{\mathbf{t}}_a - \rho_a r_a - \mathbf{i}_a \cdot \mathbf{E}_a - \dot{\mathbf{P}}_a \cdot \mathbf{E}_a - \delta_a = 0. \quad (2.13)$$

Here,  $\varepsilon_a$  is the internal energy density,  $\mathbf{T}_a$  is the stress tensor,  $\mathbf{C}_a$  is the coupling stress tensor,  $\mathbf{h}_a$  is the heat flux vector,  $\mathbf{b}_a$  is the mechanical body force density,  $q_a$  is the charge density defined by  $\rho_a z_a$ , being  $z_a$  the charge *per* unit mass,  $\mathbf{E}_a$  and  $\mathbf{P}_a$  are the electric field and the electric polarization field acting on constituent  $a$ , respectively,  $\mathbf{l}_a$  is the mechanical coupling body force density,  $\hat{\mathbf{t}}_a$  is the dual vector of  $\mathbf{T}_a$ ,  $r_a$  is the mechanical energy supply density,  $\mathbf{i}_a$  is the electric current density, and  $c_a$ ,  $\mathbf{m}_a$ ,  $\boldsymbol{\tau}_a$  and  $\delta_a$  are production terms related to the balances of mass, linear momentum, spin, and energy, respectively. Additionally, the material derivative  $d^a(\cdot)/dt$  following the motion of the constituent  $a$  is defined as  $d^a(\cdot)/dt = \partial(\cdot)/\partial t + \mathbf{v}_a \cdot \operatorname{grad}(\cdot)$ .

Complying with the principles of classical theory of mixtures laid down in [41], balance equations of the whole mixture must coincide with the balance equations of a single body, *i.e.*, a single polar body under influence of electromagnetic fields. Hence, adding up the governing Eqs. (2.10)–(2.13) over all constituents  $a = 1, \dots, n$ , one has

*Balance of mass*

$$\frac{d\rho}{dt} + \rho \operatorname{div}(\mathbf{v}) = 0, \quad (2.14)$$

*Balance of linear momentum*

$$\rho \frac{d\mathbf{v}}{dt} - \operatorname{div}(\mathbf{T}) - \rho \mathbf{b} - q \mathbf{E} - \mathbf{P} \cdot \nabla \mathbf{E} = 0, \quad (2.15)$$

*Balance of spin*

$$\rho \mathbf{I} \frac{d\boldsymbol{\omega}}{dt} - \operatorname{div}(\mathbf{C}) + 2\hat{\mathbf{t}} - \mathbf{P} \times \mathbf{E} - \rho \mathbf{l} = 0, \quad (2.16)$$

*Balance of energy*

$$\rho \frac{d\varepsilon}{dt} + \operatorname{div}(\mathbf{h}) - \mathbf{T} \cdot \nabla \mathbf{v} - \mathbf{C} \cdot \nabla \boldsymbol{\omega} - 2\boldsymbol{\omega} \cdot \hat{\mathbf{t}} - \rho r - \dot{\mathbf{P}} \cdot \mathbf{E} - \mathbf{i} \cdot \mathbf{E} = 0, \quad (2.17)$$

where the dynamic variables of the mixture are related to the partial variables by

$$\begin{aligned} \rho \mathbf{b} &= \sum_{a=1}^n \rho_a \mathbf{b}_a, & \rho \mathbf{l} &= \sum_{a=1}^n \rho_a \mathbf{l}_a, \\ \rho \mathbf{E} &= \sum_{a=1}^n \rho_a \mathbf{E}_a, & \rho \mathbf{P} &= \sum_{a=1}^n \rho_a \mathbf{P}_a, \\ \rho \varepsilon &= \sum_{a=1}^n \left( \rho_a \varepsilon_a + \frac{1}{2} \rho_a u_a^2 + \frac{1}{2} \rho_a \mathbf{s}_a \cdot \mathbf{v}_a \right), \\ \rho r &= \sum_{a=1}^n (\rho_a r_a + \mathbf{u}_a \cdot \rho_a \mathbf{b}_a + \mathbf{v}_a \cdot \rho_a \mathbf{l}_a), \end{aligned} \quad (2.18)$$

$$\begin{aligned} \mathbf{T}^T &= \sum_{a=1}^n \left( \mathbf{T}_a^T - \rho_a \mathbf{u}_a \otimes \mathbf{u}_a \right), & \mathbf{C} &= \sum_{a=1}^n (\mathbf{C}_a - \rho_a \mathbf{s}_a \otimes \mathbf{u}_a), \\ \mathbf{h} &= \sum_{a=1}^n \left\{ \mathbf{h}_a - \mathbf{T}_a^T \mathbf{u}_a - \mathbf{C}_a \mathbf{v}_a + \left[ \rho_a \varepsilon_a + \frac{1}{2} \rho_a u_a^2 + \frac{1}{2} \rho_a \mathbf{s}_a \cdot (\mathbf{v}_a - \boldsymbol{\omega}) \right] \mathbf{u}_a \right\}, \end{aligned} \quad (2.19)$$

and the sum of the production terms over all constituents is zero. Another convenient balance law, which relates the mass concentration and the diffusive fluxes of the constituents  $a$  with the barycentric velocity of the mixture, is

$$\rho \frac{d\xi_a}{dt} + \operatorname{div}(\mathbf{j}_a) - c_a = 0, \quad (2.20)$$

where  $\mathbf{j}_a \equiv \rho_a (\mathbf{v}_a - \mathbf{v})$  is the diffusive flux of the constituent  $a$  and the material derivative  $d(\cdot)/dt$  following the motion of the mixture (barycentric velocity) is defined as  $d(\cdot)/dt = \partial(\cdot)/\partial t + \mathbf{v} \cdot \operatorname{grad}(\cdot)$ .

As usual for polar material bodies, the stress tensor is not a symmetric tensor since not all torques arise from macroscopic body forces. In fact, the antisymmetry of the stress tensor is closely related to the microscopic structure of the mixture, in particular, to the torques that act on the electric dipoles of constituents. Thus, for a nonlinear electrically polarizable dielectric, if the electric field is not strong enough to keep aligned  $\mathbf{P}$  and  $\mathbf{E}$ , the stress tensor is not longer symmetric.

According to the Chu formulation of electrodynamics [15], the electric field  $\mathbf{E}$  and the magnetic field  $\mathbf{H}$  are regarded as fundamental quantities, whereas the electric displacement  $\mathbf{D}$  and the magnetic flux  $\mathbf{B}$  are auxiliary quantities. These quantities are interrelated by

$$\mathbf{D} = \varepsilon_o \mathbf{E} + \mathbf{P}, \quad \mathbf{B} = \mu_o (\mathbf{H} + \mathbf{M}), \quad (2.21)$$

where  $\varepsilon_0$  and  $\mu_0$  are, respectively, the permittivity and the permeability of free space, and  $\mathbf{M}$  is the magnetization field. Besides, if one recognizes that the time rates of change of the magnetic and magnetization fields are sufficiently low and relativistic effects are negligible, then Maxwell's equations are given in the form of

*Faraday's law*

$$\text{curl}(\mathbf{E}) = \mathbf{0}, \quad (2.22)$$

*Ampère's law*

$$\text{curl}(\mathbf{H}) = \mathbf{i} + \frac{\partial \mathbf{D}}{\partial t} + \text{curl}(\mathbf{P} \times \mathbf{v}), \quad (2.23)$$

*Gauss' law*

$$\text{div}(\mathbf{D}) = q, \quad (2.24)$$

*Magnetic flux law*

$$\text{div}(\mathbf{B}) = 0. \quad (2.25)$$

Equations (2.22)–(2.25) are the quasi-electrostatic laws of electromagnetism. In the quasi-electrostatic approximation [26], the electric field is an irrotational field, dynamic currents are small, and magnetic induction is negligible. In addition, the temporal dependence of quasi-electrostatic fields can be regarded as a secondary effect because once given the sources of electromagnetic fields at a particular instant, the fields at that same instant are determined without knowing what were their sources in earlier times. Hence, the mathematical problem of finding a quasi-static electric field for a charge distribution depending on time is equivalent to the evaluation of a succession of static fields, each one with a different charge distribution at different instants  $t$ .

### 3 Entropy principle and its consequences

In the equations presented in the last section for reacting ionic mixtures, emerging constitutive quantities must be postulated by suitable constitutive relations that must obey known universal physical principles. One can indeed reduce the generality of the constitutive relations relying upon either different formulations of the entropy principle or variational methods. In [43,44], the principle of virtual work is employed to deduce proper constitutive equations for an elastic dielectric medium under equilibrium conditions. In turn, in [36,37], Sieniutycz proposed a variational approach based on Onsager's principle for an electrochemical system under a non-stationary quasi-linear regime. Even though, despite the impressive results obtained in these works, the application of variational methods is not well posed for non-isolated systems under influence of external forces, and for systems where there exists the possibility of several coupling phenomena, such as in chemical systems [38]. In fact, it seems that reacting chemical systems do not obey the same phenomenological formalism of non-chemical ones. For instance, in electrolyte solutions, coupling between chemical reactions and non-chemical processes is very common, and one should certainly take them into account. This is a critical point in the development of a constitutive theory for reacting ionic mixtures, which requires a more comprehensive approach. Under these circumstances, the use of entropy principles is more convenient to restrict the material equations of electrolyte solutions.

For a long period, the entropy principle founded on the Clausius–Duhem inequality, whose exploitation method is based on the works of Coleman and Noll [5,42], was extensively used in the development of continuum thermodynamics to impose thermodynamic restrictions on the constitutive answers of a material body. For simple materials, the linear irreversible thermodynamics and the rational thermodynamics with the Clausius–Duhem inequality lead to the same practical results. This is the reason why the linear irreversible thermodynamics and the Clausius–Duhem inequality are still widely employed. Nevertheless, with the development of continuum theory of mixtures, it was realized [19,29,51] that the two main constitutive assumptions adopted by Coleman and Noll,

$$\Phi = \frac{\mathbf{h}}{\theta}, \quad \sigma = \frac{r}{\theta}, \quad (3.1)$$

where  $\theta$  is the absolute temperature, and  $\mathbf{h}$  and  $r$  are, respectively, the heat flux and the energy supply, are not very satisfactory for continuum mixtures. Moreover, large deviations from linear behavior are observed for chemical reactions, what restricts the application of linear irreversible thermodynamics in reacting systems. Since then, other formulations to the entropy principle have been proposed, among which the most employed one was proposed by Müller [30].



According to the Müller's proposition, the behavior of a continuum mixture and its constituents must obey the general equations

$$\begin{aligned} \rho_a \frac{d^a \eta_a}{dt} + \operatorname{div}(\Phi_a) - \rho_a \sigma_a - \rho_a \pi_a &= 0 \quad \text{for all constituents } a \\ \rho \pi &= \rho \frac{d\eta}{dt} + \operatorname{div}(\Phi) - \rho \sigma \geq 0 \quad \text{for the mixture,} \end{aligned} \quad (3.2)$$

where  $\rho \eta = \sum_{a=1}^n \rho_a \eta_a$  is the specific entropy density,  $\Phi = \sum_{a=1}^n (\Phi_a - \rho_a \eta_a \mathbf{u}_a)$  is the entropy flux,  $\rho \sigma = \sum_{a=1}^n \rho_a \sigma_a$  is the entropy supply density, and  $\rho \pi = \sum_{a=1}^n \rho_a \pi_a \geq 0$  is the entropy production density of the mixture. Note that, unlike the Coleman and Noll exploitation method of the entropy inequality,  $\Phi$  and  $\rho \sigma$  are not *a priori* assumptions, but constitutive functions on which thermodynamic restrictions must be placed. Furthermore, motivated by the Truesdell's axiom of dissipation [41], Müller assumed that the entropy production for each constituent,  $\pi_a$ , may take any value, provided the entropy production of the whole mixture,  $\pi$ , is a non-negative quantity. This assumption results in a weak limitation of the entropy principle.

Despite the Müller approach of the entropy principle is less restrictive than that proposed by Coleman and Noll, it was still very laborious, even for simple fluids and free of external supplies. Then, Liu [21] suggested to incorporate new auxiliary quantities, termed of Lagrange multipliers, to the entropy inequality in order to take into account all balance equations in the exploitation of the entropy inequality. Thanks to its comprehensive scope, nowadays the Müller–Liu approach of the entropy principle is widely employed to deduce restrictions on constitutive equations and thermodynamically consistent constitutive laws in many research fields. Some examples can be found, e.g., in references [11–13, 17, 47–50].

### 3.1 Constitutivity of electrolyte solutions

It is the purpose of this work to discuss the dynamics of aqueous electrolyte solutions. Such solutions are assumed to be diluted, so the main fluid (water) is much more dominant than all other constituents. As a result, the thermodynamics of the mixture can be described as that of the main fluid. Under these conditions, one temperature field is required.

In determining the behavior of electrochemical systems by evaluating the fields  $\rho(\mathbf{x}, t)$ ,  $\xi_a(\mathbf{x}, t)$ ,  $\mathbf{v}(\mathbf{x}, t)$ ,  $\boldsymbol{\varpi}(\mathbf{x}, t)$ ,  $\theta(\mathbf{x}, t)$ , and  $\mathbf{E}(\mathbf{x}, t)$ , one presumes that most of the effects revealed by electrochemical systems are accounted for through the dependence on the mass density, mass concentration and its gradient, velocity and its gradient, relative local angular velocity, gradient of local angular velocity, absolute temperature and its gradient, and electric field. In other words, the set of independent constitutive variables  $y$  is

$$y \in \{\rho, \xi_a, \nabla \xi_b, \mathbf{v}, \nabla \mathbf{v}, \boldsymbol{\varpi}, \nabla \boldsymbol{\varpi}, \theta, \nabla \theta, \mathbf{E}\}. \quad (\forall a, b = 1, \dots, n-1) \quad (3.3)$$

Nonetheless, as the principle of material objectivity requires that constitutive functions must be independent on the observers, constitutive functions do not depend on the velocity, and they depend on the velocity gradient only through its symmetric part, named of stretching tensor  $\mathbf{D}$ . Besides,  $\boldsymbol{\varpi}$  is also a non-objective quantity, but by using a linear map (duality map), one can establish a one-to-one correspondence between a skew-symmetric objective tensor and a non-objective vector. That is, the dependence of the constitutive functions on  $\boldsymbol{\varpi}$  occurs by means of a skew-symmetric tensor of type  $W_{ij} = e_{ijk} \varpi_k$ .

One may also exploit the irrotational nature of the quasi-static electric field and define it in terms of a scalar function. Recalling the Helmholtz theorem, one writes

$$\mathbf{E} \equiv -\nabla \varphi, \quad (3.4)$$

where  $\varphi$  is the electric potential. In other words, the electric field in quasi-electrostatics is completely specified by its scalar source only (Gauss' law).

With these assumptions, (3.3) becomes

$$y \in \{\rho, \xi_a, \nabla \xi_b, \theta, \nabla \theta, \mathbf{E}, \mathbf{D}, \mathbf{W}, \nabla \boldsymbol{\varpi}\}, \quad (\forall a, b = 1, \dots, n-1) \quad (3.5)$$

where  $\mathbf{E}$  transforms as an objective quantity in the quasi-electrostatic approximation. Incidentally, constitutive relations must be formulated for

$$\mathcal{C} \in \{\mathbf{j}_a, c_a, \mathbf{T}, \mathbf{C}, \mathbf{P}, \varepsilon, \mathbf{h}, \mathbf{i}, \eta, \Phi\}, \quad (\forall a = 1, \dots, n-1) \quad (3.6)$$



which are dependent on the variables (3.5). Through the dependence of (3.6) on (3.5), one proposes a constitutive class capable of describing the chemical changes caused by the passage of electric current, and the transport phenomena caused by electrochemical reactions in a viscous fluid. This constitutive class will characterize the material responses of a mixture of viscous polar fluids with diffusion, chemical reactions, and conduction of heat and electric current.

**Proposition 1** *The constitutive equation  $\mathcal{C} = \mathcal{C}(\mathbf{y})$ , such that  $\mathbf{y}$  and  $\mathcal{C}$  are, respectively, given by (3.5) and (3.6), defines a polar mixture of viscous fluids with heat and electrical conduction, diffusion, and chemical reactions.*

### 3.2 Derivation of thermodynamic restrictions

Once all relevant constitutive assumptions and balance equations have been established, the entropy principle can be exploited. For a physically realizable process of the mixture investigated, the entropy inequality (3.2)<sub>2</sub> must be satisfied subject to the simultaneous satisfaction of the balance laws (2.14)–(2.17), (2.20) and (2.24). Then, instead of fulfilling the entropy inequality for independent fields that are constrained by the balance laws, one employs the method of Lagrange multipliers proposed by Liu [21]. According to this approach, the entropy inequality is subtracted from the products of each balance equation with its corresponding Lagrange multiplier, so that it can be satisfied for unrestricted independent fields. For the mixture investigated, the extended entropy inequality

$$\begin{aligned} \Pi = & \rho \frac{d\eta}{dt} + \operatorname{div}(\Phi) - \rho\sigma - \Lambda^\rho \left( \frac{d\rho}{dt} + \rho \operatorname{div}(\mathbf{v}) \right) - \Lambda^{\mathbf{v}} \cdot \left( \rho \frac{d\mathbf{v}}{dt} - \operatorname{div}(\mathbf{T}) - q\mathbf{E} - \rho\mathbf{b} - \mathbf{P} \cdot \nabla \mathbf{E} \right) \\ & - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \left( \rho \frac{d\xi_a}{dt} + \operatorname{div}(\mathbf{j}_a) - c_a \right) - \Lambda^\omega \cdot \left( \rho \mathbf{I} \frac{d\boldsymbol{\omega}}{dt} - \operatorname{div}(\mathbf{C}) + 2\hat{\mathbf{t}} - \rho\mathbf{l} - \mathbf{P} \times \mathbf{E} \right) \\ & - \Lambda^\varepsilon \left( \rho \frac{d\varepsilon}{dt} + \operatorname{div}(\mathbf{h}) - \mathbf{T} \cdot \nabla \mathbf{v} - \mathbf{C} \cdot \nabla \boldsymbol{\omega} - 2\boldsymbol{\omega} \cdot \hat{\mathbf{t}} - \rho r - \dot{\mathbf{P}} \cdot \mathbf{E} - \mathbf{i} \cdot \mathbf{E} \right) \\ & - \Lambda^G (\operatorname{div}(\mathbf{P}) - \varepsilon_o \operatorname{div}(\mathbf{E}) - q) \geq 0 \end{aligned} \quad (3.7)$$

holds for any values of  $\rho(\mathbf{x}, t)$ ,  $\xi_a(\mathbf{x}, t)$ ,  $\mathbf{v}(\mathbf{x}, t)$ ,  $\boldsymbol{\omega}(\mathbf{x}, t)$ ,  $\theta(\mathbf{x}, t)$  and  $\mathbf{E}(\mathbf{x}, t)$ , where  $\varepsilon_o$  is homogeneous. Here, the quantities  $\Lambda^\rho$ ,  $\Lambda^{\mathbf{v}}$ ,  $\Lambda^{\xi_a}$ ,  $\Lambda^\omega$ ,  $\Lambda^\varepsilon$ , and  $\Lambda^G$  represent the Lagrange multipliers associated with the constraints placed on the entropy inequality by the balance equations. These Lagrange multipliers may be given by constitutive relations too.

In addition to previous constitutive assumptions, some further premises must be taken into account, most of which are plausible. They are as follows:

- For many materials whose constitutive class does not encompass the time derivative of temperature,  $d\theta/dt$ , in the set of independent constitutive variables, and the heat flux is collinear to the entropy flux, the Lagrange multiplier of energy is the reciprocal of the temperature,  $\Lambda^\varepsilon = 1/\theta$ , also referred as coldness [17, 24, 48]. Nonetheless,  $\Lambda^\varepsilon = 1/\theta$  is a feasible hypothesis for the constitutive class presented in this work, although in this case the entropy flux is not collinear to the heat flux. This will be shown in the appendix.
- The definition of  $\Lambda^{\xi_a}$  can be obtained by taking into account a semipermeable membrane, which separates the reacting ionic mixture and one of its constituents  $a$  [17, 22]. Excluding the possibility of tangential velocities at the wall, and by assuming that the temperature is continuous at the membrane, one obtains the following jump expression,

$$\left[ \left[ -\frac{\Lambda^{\xi_a}}{\Lambda^\varepsilon} + \frac{1}{2} (\mathbf{v}_a - u\mathbf{n})^2 \right] \right] = 0,$$

where  $\mathbf{n}$  is a unit normal vector to the membrane, and  $u$  is the membrane speed. The first term on the left-hand side of the expression above is named chemical potential,  $\mu_a$ , whereas the second one is the kinetic energy of the motion of constituent  $a$  in relation to the semipermeable wall. Clearly, only the chemical potential is a constitutive quantity, and it is easily related to the Lagrange multiplier of mass concentration by  $\mu_a = -\Lambda^{\xi_a}/\Lambda^\varepsilon$ ;

- The definition of  $\Lambda^\rho$  comes from the evaluation of equilibrium conditions for a viscous heat-conducting fluid, *i.e.*,  $p = -\rho\Lambda^\rho/\Lambda^\varepsilon$  [17,24,48]. Then, because of the great excess of solvent mass in relation to the constituents' masses, the dynamics of a reacting ionic mixture is nearly the same as for a viscous heat-conducting fluid. Consequently, one may use the previous definition without loss of generality;
- The material properties of a reacting ionic mixture are independent on the supplies, and the entropy source is a linear combination of the supplies of linear momentum, spin, and energy, *i.e.*,

$$\rho\sigma = \mathbf{\Lambda}^v \cdot \rho\mathbf{b} + \mathbf{\Lambda}^\omega \cdot \rho\mathbf{l} + \Lambda^\varepsilon \rho r$$

With this assumption,  $\mathbf{\Lambda}^v$ ,  $\mathbf{\Lambda}^\omega$  and  $\Lambda^\varepsilon$  do not depend on the source terms, and  $\rho\sigma$  must vanish in the entropy inequality;

- The mixture is an isotropic and linear medium. Although, exceptionally, the degree of polarization of the electrolyte solution and its constituents is completely determined by a non-linear anisotropic function of type  $P_i = \gamma_{ij}^1 E_j + \gamma_{ijk}^2 E_j E_k + \gamma_{ijkl}^3 E_j E_k E_l + \dots$ , where  $\gamma^n$  is the  $n$ -th order electric susceptibility. In general, for weak electric fields,  $\gamma^n$  is a constant characteristic of the dielectric medium and it depends on the temperature since thermal agitation tends to oppose the ordering of electric dipoles induced by  $\mathbf{E}$ . Thus, owing the great excess of solvent mass in relation to the masses of the remaining constituents, the dielectric properties of the whole solution are due almost exclusively to the electric dipoles of water molecules.

Substituting the constitutive relations (3.5) and (3.6) into Eq. (3.7) and by performing all required differentiations according to the chain rule, one obtains

$$\begin{aligned} \Pi = & \frac{d\rho}{dt} \left( \rho \frac{\partial \eta}{\partial \rho} - \Lambda^\rho - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \rho} \right) \\ & + \sum_{a=1}^{n-1} \frac{d\xi_a}{dt} \left( \rho \frac{\partial \eta}{\partial \xi_a} - \rho \Lambda^{\xi_a} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \xi_a} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \xi_a} \right) \\ & + \sum_{b=1}^{n-1} \frac{d\nabla \xi_b}{dt} \cdot \left( \rho \frac{\partial \eta}{\partial \nabla \xi_b} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \xi_b} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \nabla \xi_b} \right) \\ & + \frac{d\mathbf{W}}{dt} \cdot \left( \rho \frac{\partial \eta}{\partial \mathbf{W}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{W}} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \mathbf{W}} \right) + \frac{d\omega}{dt} \cdot (-\rho \mathbf{l} \Lambda^\omega) \\ & + \frac{d\nabla \omega}{dt} \cdot \left( \rho \frac{\partial \eta}{\partial \nabla \omega} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \omega} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \nabla \omega} \right) \\ & + \frac{d\theta}{dt} \left( \rho \frac{\partial \eta}{\partial \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \theta} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \theta} \right) \\ & + \frac{d\nabla \theta}{dt} \cdot \left( \rho \frac{\partial \eta}{\partial \nabla \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \theta} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \nabla \theta} \right) \\ & + \frac{d\mathbf{E}}{dt} \cdot \left( \rho \frac{\partial \eta}{\partial \mathbf{E}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{E}} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \mathbf{E}} \right) \\ & + \frac{d\mathbf{D}}{dt} \cdot \left( \rho \frac{\partial \eta}{\partial \mathbf{D}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{D}} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \mathbf{D}} \right) + \frac{d\mathbf{v}}{dt} \cdot (-\rho \mathbf{\Lambda}^v) \\ & + \nabla \rho \cdot \left( \frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \mathbf{\Lambda}^v \frac{\partial \mathbf{T}}{\partial \rho} + \mathbf{\Lambda}^\omega \frac{\partial \mathbf{C}}{\partial \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} \right) \\ & + \sum_{b=1}^{n-1} \nabla \xi_b \cdot \left( \frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} + \mathbf{\Lambda}^v \frac{\partial \mathbf{T}}{\partial \xi_b} + \mathbf{\Lambda}^\omega \frac{\partial \mathbf{C}}{\partial \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} \right) \\ & + \sum_{b=1}^{n-1} \nabla (\nabla \xi_b) \cdot \left( \frac{\partial \Phi}{\partial \nabla \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \xi_b} + \mathbf{\Lambda}^v \frac{\partial \mathbf{T}}{\partial \nabla \xi_b} + \mathbf{\Lambda}^\omega \frac{\partial \mathbf{C}}{\partial \nabla \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \xi_b} \right) \end{aligned}$$

$$\begin{aligned}
& +\nabla \mathbf{W} \cdot \left( \frac{\partial \Phi}{\partial \mathbf{W}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{W}} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \mathbf{W}} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \mathbf{W}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{W}} - \Lambda^{\varepsilon} \frac{\partial \mathbf{h}}{\partial \mathbf{W}} \right) \\
& +\nabla (\nabla \omega) \cdot \left( \frac{\partial \Phi}{\partial \nabla \omega} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \omega} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \nabla \omega} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \nabla \omega} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \omega} - \Lambda^{\varepsilon} \frac{\partial \mathbf{h}}{\partial \nabla \omega} \right) \\
& +\nabla \theta \cdot \left( \frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \theta} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^{\varepsilon} \frac{\partial \mathbf{h}}{\partial \theta} \right) \\
& +\nabla (\nabla \theta) \cdot \left( \frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \nabla \theta} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \nabla \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^{\varepsilon} \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) \\
& +\nabla \mathbf{E} \cdot \left( \frac{\partial \Phi}{\partial \mathbf{E}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{E}} + \Lambda^{\mathbf{v}} \cdot \mathbf{P} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \mathbf{E}} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \mathbf{E}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{E}} - \Lambda^{\varepsilon} \frac{\partial \mathbf{h}}{\partial \mathbf{E}} \right) \\
& +\nabla \mathbf{D} \cdot \left( \frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \mathbf{D}} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \mathbf{D}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^{\varepsilon} \frac{\partial \mathbf{h}}{\partial \mathbf{D}} \right) \\
& -2\Lambda^{\omega} \cdot \hat{\mathbf{t}} + \Lambda^{\omega} \cdot (\mathbf{P} \times \mathbf{E}) + \Lambda^{\varepsilon} \mathbf{T} \cdot \mathbf{D} + 2\Lambda^{\varepsilon} \hat{\mathbf{t}} \cdot \omega - \rho \Lambda^{\rho} \mathbf{1} \cdot \mathbf{D} \\
& +\Lambda^G \varepsilon_o \operatorname{div}(\mathbf{E}) + \Lambda^G q + \Lambda^{\varepsilon} \mathbf{C} \cdot \nabla \omega + \sum_{a=1}^{n-1} \Lambda^{\xi_a} c_a + \Lambda^{\varepsilon} \mathbf{i} \cdot \mathbf{E} \geq 0.
\end{aligned} \tag{3.8}$$

Alternatively, Eq.(3.8) can be expressed as

$$\Pi = \mathbf{A}(\mathbf{y}) \cdot \mathbf{X} + B(\mathbf{y}) \geq 0, \tag{3.9}$$

where  $\mathbf{A}(\mathbf{y})$  and  $B(\mathbf{y})$  are, respectively, vector and scalar functions of the variables  $\mathbf{y}$  listed in (3.5), but not of  $\mathbf{X}$ :

$$\begin{aligned}
\mathbf{X} \in \left\{ \frac{d\rho}{dt}, \frac{d\xi_a}{dt}, \frac{d\nabla \xi_b}{dt}, \frac{d\theta}{dt}, \frac{d\nabla \theta}{dt}, \frac{d\mathbf{W}}{dt}, \frac{d\omega}{dt}, \frac{d\nabla \omega}{dt}, \frac{d\mathbf{E}}{dt}, \frac{d\mathbf{D}}{dt}, \frac{d\mathbf{v}}{dt}, \nabla \rho, \right. \\
\left. \nabla (\nabla \xi_b), \nabla (\nabla \theta), \nabla \mathbf{E}, \nabla \mathbf{D}, \nabla \mathbf{W}, \nabla (\nabla \omega), \operatorname{div}(\mathbf{E}) \right\}.
\end{aligned} \tag{3.10}$$

Hence, Liu [24] demonstrated by the principle of local solvability that the inequality (3.9) is linear in (3.10) and it must hold for arbitrary values of  $\mathbf{y}$  and  $\mathbf{X}$ . Necessary and sufficient condition for this is

$$\mathbf{A}(\mathbf{y}) = \mathbf{0}, \quad B(\mathbf{y}) \geq 0. \tag{3.11}$$

In other terms, (3.11) indicates that the coefficients of  $\mathbf{X}$  must vanish, otherwise Eq.(3.9) could be violated. These arguments lead to the following Liu identities

$$\begin{aligned}
\rho \frac{\partial \eta}{\partial \rho} - \Lambda^{\rho} - \rho \Lambda^{\varepsilon} \frac{\partial \varepsilon}{\partial \rho} + \Lambda^{\varepsilon} \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \rho} &= 0, \\
\rho \frac{\partial \eta}{\partial \xi_a} - \rho \Lambda^{\xi_a} - \rho \Lambda^{\varepsilon} \frac{\partial \varepsilon}{\partial \xi_a} + \Lambda^{\varepsilon} \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \xi_a} &= 0, \quad (\forall a = 1, \dots, n-1) \\
\rho \frac{\partial \eta}{\partial \nabla \xi_b} - \rho \Lambda^{\varepsilon} \frac{\partial \varepsilon}{\partial \nabla \xi_b} + \Lambda^{\varepsilon} \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \nabla \xi_b} &= 0, \quad (\forall b = 1, \dots, n-1) \\
\rho \frac{\partial \eta}{\partial \mathbf{W}} - \rho \Lambda^{\varepsilon} \frac{\partial \varepsilon}{\partial \mathbf{W}} + \Lambda^{\varepsilon} \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \mathbf{W}} &= \mathbf{0}, \\
\rho \frac{\partial \eta}{\partial \nabla \omega} - \rho \Lambda^{\varepsilon} \frac{\partial \varepsilon}{\partial \nabla \omega} + \Lambda^{\varepsilon} \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \nabla \omega} &= \mathbf{0}, \\
\rho \frac{\partial \eta}{\partial \theta} - \rho \Lambda^{\varepsilon} \frac{\partial \varepsilon}{\partial \theta} + \Lambda^{\varepsilon} \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \theta} &= 0,
\end{aligned} \tag{3.12}$$

$$\begin{aligned}\rho \frac{\partial \eta}{\partial \nabla \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \theta} + \Lambda^\varepsilon \mathbf{E} \frac{\partial \mathbf{P}}{\partial \nabla \theta} &= \mathbf{0}, \\ \rho \frac{\partial \eta}{\partial \mathbf{E}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{E}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial \mathbf{P}}{\partial \mathbf{E}} &= \mathbf{0}, \\ \rho \frac{\partial \eta}{\partial \mathbf{D}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{D}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial \mathbf{P}}{\partial \mathbf{D}} &= \mathbf{0}, \\ -\rho \mathbf{I} \mathbf{A}^\omega &= \mathbf{0}, \quad -\rho \mathbf{A}^\nu = \mathbf{0}, \quad \Lambda^G = 0,\end{aligned}$$

$$\begin{aligned}\frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \mathbf{A}^\nu \frac{\partial \mathbf{T}}{\partial \rho} + \mathbf{A}^\omega \frac{\partial \mathbf{C}}{\partial \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} &= \mathbf{0}, \\ \text{sym} \left( \frac{\partial \Phi}{\partial \nabla \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \xi_b} + \mathbf{A}^\nu \frac{\partial \mathbf{T}}{\partial \nabla \xi_b} + \mathbf{A}^\omega \frac{\partial \mathbf{C}}{\partial \nabla \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \xi_b} \right) &= \mathbf{0}, \quad (\forall b = 1, \dots, n-1) \\ \frac{\partial \Phi}{\partial \mathbf{W}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{W}} + \mathbf{A}^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{W}} + \mathbf{A}^\omega \frac{\partial \mathbf{C}}{\partial \mathbf{W}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{W}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{W}} &= \mathbf{0}, \\ \frac{\partial \Phi}{\partial \nabla \omega} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \omega} + \mathbf{A}^\nu \frac{\partial \mathbf{T}}{\partial \nabla \omega} + \mathbf{A}^\omega \frac{\partial \mathbf{C}}{\partial \nabla \omega} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \omega} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \omega} &= \mathbf{0}, \\ \text{sym} \left( \frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \mathbf{A}^\nu \frac{\partial \mathbf{T}}{\partial \nabla \theta} + \mathbf{A}^\omega \frac{\partial \mathbf{C}}{\partial \nabla \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) &= \mathbf{0}, \\ \frac{\partial \Phi}{\partial \mathbf{E}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{E}} + \mathbf{A}^\nu \cdot \mathbf{P} + \mathbf{A}^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{E}} + \mathbf{A}^\omega \frac{\partial \mathbf{C}}{\partial \mathbf{E}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{E}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{E}} &= \mathbf{0}, \\ \frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \mathbf{A}^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{D}} + \mathbf{A}^\omega \frac{\partial \mathbf{C}}{\partial \mathbf{D}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} &= \mathbf{0},\end{aligned} \tag{3.13}$$

whence certain thermodynamic relations are expected to maintain, namely:

1. The thermodynamic potential,  $\psi = \varepsilon - \theta \eta - \frac{1}{\rho} \mathbf{P} \cdot \mathbf{E}$ , is function only of  $\rho$ ,  $\xi_a$ ,  $\theta$ , and  $\mathbf{E}$ .
2. The Lagrange multipliers of the balance equations of linear momentum, spin, and Gauss law are zero:

$$\mathbf{A}^\nu = \mathbf{0}, \quad \mathbf{A}^\omega = \mathbf{0}, \quad \Lambda^G = 0.$$

3. The extra entropy flux vector,  $\phi = \Phi - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a - \Lambda^\varepsilon \mathbf{h}$ , which accounts all deviations of the entropy flux vector in relation to the heat and diffusive flux vectors, does not amount to a restriction.

The first statement follows from Eqs.(3.12)<sub>3,4,5,7,9</sub>, which demonstrate a reduced independence on the proposed list (3.5) for the thermodynamic potential  $\psi$ . Then, with the aid of the thermodynamic potential  $\psi$ , and the definitions of hydrostatic pressure,  $p = -\rho \Lambda^\rho / \Lambda^\varepsilon$ , chemical potential,  $\mu_a = -\Lambda^{\xi_a} / \Lambda^\varepsilon$ , and coldness,  $\Lambda^\varepsilon = 1/\theta$ , the relations (3.12)<sub>1,2,6,8</sub> yield

$$d\psi = \frac{p}{\rho^2} d\rho + \sum_{a=1}^{n-1} \mu_a d\xi_a - \eta d\theta - \mathbf{P} \cdot d(\mathbf{E}/\rho), \tag{3.14}$$

whence  $\partial \psi / \partial \rho = p/\rho^2 + \mathbf{P} \cdot \mathbf{E}/\rho^2$ ,  $\partial \psi / \partial \xi_a = \mu_a$ ,  $\partial \psi / \partial \theta = -\eta$ , and  $\partial \psi / \partial \mathbf{E} = -\mathbf{P}/\rho$ . If electromagnetic fields are absent, (3.14) coincides with the Helmholtz relation of the classical thermostatics. However, the former is more comprehensive than that of classical thermostatics because it holds for any point of the material body and it is valid under equilibrium and non-equilibrium conditions.

Moreover, in view of the previous constitutive assumptions presented in Subsect. 3.1, one demonstrates by cross-differentiation of the Liu identities (3.12)<sub>1,2,6,8</sub> that  $\eta = \hat{\eta}(\rho, \theta, \xi_a)$ ,  $\varepsilon = \hat{\varepsilon}(\rho, \theta, \xi_a)$ ,  $\Lambda^\rho =$

$\hat{\Lambda}^\rho(\rho, \theta, \xi_a)$ , and  $\Lambda^{\xi_a} = \hat{\Lambda}^{\xi_a}(\rho, \theta, \xi_a)$ . One also shows from (3.14) and the reduced dependencies above that the integrability conditions for  $d\psi$  are

$$\frac{\partial \mu_a}{\partial \rho} = \frac{\partial (p/\rho^2)}{\partial \xi_a}, \quad \frac{\partial (p/\rho^2)}{\partial \theta} = -\frac{\partial \eta}{\partial \rho}, \quad \frac{\partial \mu_a}{\partial \theta} = -\frac{\partial \eta}{\partial \xi_a}, \quad (3.15)$$

where it was considered that  $\mathbf{P}$  is function only of  $\mathbf{E}$ , as previously stated.

The second statement is a direct result of Eq. (3.12)<sub>10</sub> and it does not deserve additional comments. On the other hand, the third statement results from Eq. (3.13), which suggests the introduction of an extra entropy flux defined by  $\phi = \Phi - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a - \Lambda^\varepsilon \mathbf{h}$ . Here, it is worthwhile to remember that in obtaining Eqs. (3.13)<sub>2,5</sub>, the theorem of Cartesian decomposition of tensors was used in order to impose that only the symmetric parts of  $\nabla(\nabla \xi_b)$ , and  $\nabla(\nabla \theta)$  need to vanish. The proof of this statement can be easily found in [24].

Substituting the definition of the extra entropy flux into Eq. (3.13), it results in

$$\begin{aligned} \frac{\partial \phi}{\partial \rho} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \rho} \mathbf{j}_a, & \text{sym} \left( \frac{\partial \phi}{\partial \nabla \xi_b} \right) &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \xi_b} \mathbf{j}_a, & (\forall b = 1, \dots, n-1) \\ \frac{\partial \phi}{\partial \mathbf{W}} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \mathbf{W}} \mathbf{j}_a, & \frac{\partial \phi}{\partial \nabla \omega} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \omega} \mathbf{j}_a, \\ \text{sym} \left( \frac{\partial \phi}{\partial \nabla \theta} \right) &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \theta} \mathbf{j}_a, & \frac{\partial \phi}{\partial \mathbf{E}} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \mathbf{E}} \mathbf{j}_a, \\ \frac{\partial \phi}{\partial \mathbf{D}} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \mathbf{D}} \mathbf{j}_a. \end{aligned} \quad (3.16)$$

With the definition  $\mu_a = -\Lambda^{\xi_a}/\Lambda^\varepsilon$ , the reduced dependence of  $\Lambda^{\xi_a}$  should be reflected in  $\mu_a$  and, then,  $\mu_a = \hat{\mu}_a(\rho, \theta, \xi_a)$ . Consequently, some of the derivatives above must vanish, namely  $\text{sym} \left( \frac{\partial \phi}{\partial \nabla \xi_b} \right) = \mathbf{0}$ ,  $\frac{\partial \phi}{\partial \mathbf{W}} = \mathbf{0}$ ,  $\frac{\partial \phi}{\partial \nabla \omega} = \mathbf{0}$ ,  $\text{sym} \left( \frac{\partial \phi}{\partial \nabla \theta} \right) = \mathbf{0}$ ,  $\frac{\partial \phi}{\partial \mathbf{E}} = \mathbf{0}$  and  $\frac{\partial \phi}{\partial \mathbf{D}} = \mathbf{0}$ , but not  $\frac{\partial \phi}{\partial \rho}$ . Nonetheless, if one considers that  $\phi$  is an isotropic vector function, from the theorem of representation of isotropic functions [45, 46], the extra entropy flux is zero because there is no isotropic vector function whose set of generators encompasses scalars and second-rank tensors. Therefore,  $\Phi$  can be rewritten as  $\Phi = \Lambda^\varepsilon \mathbf{h} - \Lambda^\varepsilon \sum_{a=1}^{n-1} \mu_a \mathbf{j}_a$ .

After elimination of the linear terms, one uses  $\nabla \mu_a = \sum_{b=1}^{n-1} \frac{\partial \mu_a}{\partial \xi_b} \nabla \mu_b + \frac{\partial \mu_a}{\partial \theta} \nabla \theta$ , where  $\nabla \rho$  was omitted due to the constitutive assumptions, and  $\Phi = \Lambda^\varepsilon \mathbf{h} - \Lambda^\varepsilon \sum_{a=1}^{n-1} \mu_a \mathbf{j}_a$  to rewrite Eq. (3.8) as

$$\Pi = - \sum_{a=1}^{n-1} \mathbf{j}_a \cdot \nabla \mu_a + \left( \sum_{a=1}^{n-1} \mathbf{j}_a \mu_a - \mathbf{h} \right) \cdot \frac{\nabla \theta}{\theta} + \mathbf{C} \cdot \nabla \omega + \mathbf{T} \cdot \mathbf{D} + p \mathbf{1} \cdot \mathbf{D} - \sum_{a=1}^{n-1} \mu_a c_a + \mathbf{i} \cdot \mathbf{E} \geq 0, \quad (3.17)$$

whence one may obtain other important thermodynamic restrictions on the constitutive relations.

Nevertheless, before discussing the consequences of Eq. (3.17) on the constitutive functions listed in (3.6), an important concept of chemical thermodynamics deserves to be presented. The chemical affinity of a reaction  $r$  is

$$\mathcal{U}_r = \sum_{a=1}^{n-1} v_{ar} \mu_a, \quad (3.18)$$

where  $v_{ar}$  divided by the molecular mass of constituent  $a$  is proportional to the corresponding stoichiometric coefficient in the chemical reaction  $r$ , and the solvent is regarded as inert because of its great excess in the mixture. In addition, in agreement with Bedford and Bowen's ideas [1, 3], the mass production of  $a$  is the net rate of mass supply to the constituent  $a$  resulting from chemical reactions. Mathematically, the mass production of constituent  $a$  is expressed by

$$c_a = \sum_{r=1}^R v_{ar} \gamma_r, \quad (3.19)$$

where  $\Upsilon_r$  is the rate of conversion of  $r$ , supposing  $R$  independent chemical reactions. Combining Eqs. (3.18) and (3.19), one writes  $\sum_{a=1}^{n-1} c_a \mu_a = \sum_{r=1}^R \bar{\mathcal{U}}_r \Upsilon_r$  and Eq. (3.17) reduces to

$$\Pi = - \sum_{a=1}^{n-1} \mathbf{j}_a \cdot \nabla \mu_a + \left( \sum_{a=1}^{n-1} \mathbf{j}_a \mu_a - \mathbf{h} \right) \cdot \frac{\nabla \theta}{\theta} + \mathbf{C} \cdot \nabla \omega + \mathbf{T} \cdot \mathbf{D} + p \mathbf{1} \cdot \mathbf{D} - \sum_{r=1}^R \bar{\mathcal{U}}_r \Upsilon_r + \mathbf{i} \cdot \mathbf{E} \geq 0. \quad (3.20)$$

Eq. (3.20) is the residual entropy production and it comprises a necessary condition to Eq. (3.7) holds for any solution  $\{\rho(\mathbf{x}, t), \xi_a(\mathbf{x}, t), \mathbf{v}(\mathbf{x}, t), \omega(\mathbf{x}, t), \theta(\mathbf{x}, t), \mathbf{E}(\mathbf{x}, t)\}$  of the field equations.

**Proposition 2** *If the extra entropy flux vector is zero, necessary and sufficient condition for the inequality (3.7) not to be violated for all independent variations of (3.10) is*

$$\begin{aligned} \varepsilon &= \varepsilon(\rho, \theta, \xi_a), \quad \eta = \eta(\rho, \theta, \xi_a), \quad \psi = \psi(\rho, \theta, \xi_a, \mathbf{E}), \\ \Lambda^{\xi_a} &= \Lambda^{\xi_a}(\rho, \theta, \xi_a), \quad \Lambda^\rho = \Lambda^\rho(\rho, \theta, \xi_a), \\ &- \sum_{a=1}^{n-1} \mathbf{j}_a \cdot \nabla \mu_a + \left( \sum_{a=1}^{n-1} \mathbf{j}_a \mu_a - \mathbf{h} \right) \cdot \frac{\nabla \theta}{\theta} + \mathbf{C} \cdot \nabla \omega + \mathbf{T} \cdot \mathbf{D} + p \mathbf{1} \cdot \mathbf{D} - \sum_{r=1}^R \bar{\mathcal{U}}_r \Upsilon_r + \mathbf{i} \cdot \mathbf{E} \geq 0, \end{aligned}$$

where  $a = 1, \dots, n-1$ .

### 3.2.1 Local equilibrium restrictions

The thermodynamic equilibrium state at  $(\mathbf{x}, t)$  of a reacting ionic mixture is defined as that thermodynamic state in which the residual entropy production attains the minimum value, expressly zero. This definition of thermodynamic equilibrium state does not require that the quantities  $\zeta \in \{\Upsilon_r, \nabla \theta, \nabla \mu_a, \mathbf{E}, \nabla \omega, \mathbf{D}\}$  are time independent, neither spatially homogeneous nor null. For chemical and biological systems, in general, time independence and spatial homogeneity of  $\zeta$  or even  $\zeta = 0$  are considered as being too restrictive equilibrium conditions, particularly when chemical reactions are taken into account. For this reason, in this work, it is imposed that  $\Pi$  must satisfy the weaker conditions

$$\begin{aligned} \Pi : \zeta \rightarrow Y \mid \zeta \in \{\Upsilon_r, \nabla \theta, \nabla \mu_a, \mathbf{E}, \nabla \omega, \mathbf{D}\}, \\ \left( \frac{\partial \Pi}{\partial \zeta} \right) \Big|_E = 0, \quad \left( \frac{\partial^2 \Pi}{\partial \zeta \partial \zeta} \right) \Big|_E \text{ is non-negative definite}, \end{aligned} \quad (3.21)$$

where the index  $E$  stands for local equilibrium state.

From (3.20) and (3.21), the first-order derivatives of  $\Pi$  with relation to  $\nabla \mu_a, \nabla \theta$ , and  $\nabla \omega$  results in

$$\left( \frac{\partial \Pi}{\partial \nabla \mu_a} \right) \Big|_E = -\mathbf{j}_a = \mathbf{0}, \quad (\forall a = 1, \dots, n-1) \quad (3.22)$$

$$\left( \frac{\partial \Pi}{\partial \nabla \theta} \right) \Big|_E = \frac{1}{\theta} \left( \sum_{a=1}^{n-1} \mathbf{j}_a \mu_a - \mathbf{h} \right) = \mathbf{0}, \quad (3.23)$$

or yet

$$\left( \frac{\partial \Pi}{\partial \nabla \theta} \right) \Big|_E = -\frac{1}{\theta} \mathbf{h} = \mathbf{0},$$

and

$$\left( \frac{\partial \Pi}{\partial \nabla \omega} \right) \Big|_E = \mathbf{C} = \mathbf{0}. \quad (3.24)$$

Hence, at the local equilibrium, there are no diffusive fluxes of species, neither flux of heat nor coupling stresses. Moreover, for  $\Upsilon_r$ , (3.20) and (3.21) lead to

$$\left( \frac{\partial \Pi}{\partial \Upsilon_r} \right) \Big|_E = -\bar{\mathcal{U}}_r = 0, \quad (\forall r = 1, \dots, R) \quad (3.25)$$

where the result above is the known local chemical equilibrium condition.

Other conditions to ensure  $\Pi = 0$  at  $(\mathbf{x}, t)$  are

$$\left( \frac{\partial \Pi}{\partial \mathbf{D}} \right) \Big|_E = \mathbf{T} + p\mathbf{1} = \mathbf{0}, \quad (3.26)$$

that produces

$$\mathbf{T} = -p\mathbf{1},$$

and

$$\left( \frac{\partial \Pi}{\partial \mathbf{E}} \right) \Big|_E = \mathbf{i} = \mathbf{0}. \quad (3.27)$$

**Proposition 3** *Necessary conditions for a reacting ionic mixture reaches the thermodynamic equilibrium state are*

$$\begin{aligned} \mathbf{j}_a &= \mathbf{0}, & \mathbf{h} &= \mathbf{0}, & \mathbf{i} &= \mathbf{0}, \\ \bar{\mathcal{U}}_r &= 0, & \mathbf{T} &= -p\mathbf{1}, & \mathbf{C} &= \mathbf{0}, \end{aligned}$$

where  $a = 1, \dots, n-1$  and  $r = 1, \dots, R$ .

The constitutive modeling of reacting ionic mixtures proceeds by analyzing the second restriction put by the entropy principle on (3.6) to find restrictions on phenomenological parameters. For the sake of simplicity, in addition to previous constitutive assumptions, it is imposed that the microscopic structure of the system does not influence the diffusive fluxes neither the electric current flow. Thus, the influence of local angular motion has been only considered on the stress tensor, coupling stress tensor, and the heat flux, such as in [4].

In addition, unlike common electrolyte models, the fluxes of heat, mass, and electric current are not given exclusively by their usual sources, but also by the cross-phenomena of thermoelectricity, thermal diffusion, and electrophoresis. Therefore, considering the linear representation of isotropic constitutive functions [45, 46], it follows

$$\begin{aligned} T_{ij} &= -p\delta_{ij} + \left( \lambda + \frac{2}{3}\tau \right) D_{mm}\delta_{ij} + 2\tau \bar{D}_{ij} + 2\chi e_{ijk}\varpi_k, \\ C_{ij} &= \left( \alpha + \frac{2}{3}\beta \right) \omega_{k,k}\delta_{ij} + 2\beta \bar{\omega}_{i,j} + \gamma \omega_{j,i} + \varsigma e_{ijk}\theta_{,k}, \\ h_i &= k_1\theta_{,i} + k_2E_i + k_3\mu_{,i}^a + k_4e_{ijk}\omega_{k,j}, \\ i_i &= \iota_1\theta_{,i} + \iota_2E_i + \iota_3\mu_{,i}^a, \\ j_i^a &= C_1^a\theta_{,i} + C_2^aE_i + C_3^a\mu_{,i}^a, \end{aligned} \quad (3.28)$$

where  $\bar{D}_{ij}$  and  $\bar{\omega}_{i,j}$  are, respectively, the deviatoric part of  $\mathbf{D}$  and  $\nabla \boldsymbol{\omega}$  and all phenomenological coefficients are functions of  $\rho, \theta, \xi_a, \nabla \xi_a \cdot \nabla \xi_a, \nabla \theta \cdot \nabla \theta, \mathbf{E} \cdot \mathbf{E}, \nabla \xi_a \cdot \nabla \theta, \nabla \xi_a \cdot \mathbf{E}, \nabla \theta \cdot \mathbf{E}$ , and  $\text{tr} \mathbf{D}$ . Obviously, despite their inherent simplicity, in general, these constitutive functions are suitable to describe the diffusive and advective structures of electrolyte solutions far from the equilibrium. Nonetheless, as de Groot and Mazur [10] pointed out, the linear approximation for chemical reactions is not justifiable, except near an equilibrium state when the chemical affinity holds a reciprocal relation with the rate of conversion of  $r$ . On the other hand, far from the equilibrium, chemical affinity is essentially a nonlinear function of  $\mathcal{V}_r$  and its form varies according to the reaction complexity. In fact, the task of determining a phenomenological equation for  $\bar{\mathcal{U}}_r$  is quite complicated and unusual in Chemistry. Then, on account of these arguments, chemical affinity is treated only in general terms, without specifying its constitutive nature.

Inserting Eq. (3.28) into Eq. (3.20), the residual entropy inequality becomes

$$\begin{aligned} \Pi &= - \sum_{a=1}^{n-1} (C_1^a\theta_{,i} + C_2^aE_i + C_3^a\mu_{,i}^a) \mu_{,i}^a + \sum_{a=1}^{n-1} (C_1^a\theta_{,i} + C_2^aE_i + C_3^a\mu_{,i}^a) \mu^a \frac{\theta_{,i}}{\theta} \\ &\quad - (k_1\theta_{,i} + k_2E_i + k_3\mu_{,i}^a + k_4e_{ijk}\omega_{k,j}) \frac{\theta_{,i}}{\theta} + \left( \lambda + \frac{2}{3}\tau \right) D_{mm}^2 + 2\tau \bar{D}_{ik}\bar{D}_{ik} + 2\chi e_{ijk}\omega_k D_{ij} \end{aligned}$$



$$\begin{aligned}
 & + \left( \alpha + \frac{2}{3} \beta \right) \omega_{k,k}^2 + 2\beta \bar{\omega}_{i,j} \bar{\omega}_{i,j} + \gamma \omega_{j,i} \omega_{j,i} + \varsigma e_{ijk} \theta_{,k} \omega_{i,j} \\
 & - \sum_{r=1}^R \bar{U}_r \gamma_r - (\iota_1 \theta_{,i} + \iota_2 E_i + \iota_3 \mu_{,i}^a) E_i \geq 0,
 \end{aligned} \tag{3.29}$$

and by performing the second-order derivatives of  $\Pi$  with respect to the variables listed in the set  $\zeta$ , it results in

$$\begin{aligned}
 & \sum_{a=1}^{n-1} C_3^a \leq 0, \quad \frac{1}{\theta} \sum_{a=1}^{n-1} C_1^a \mu^a + \frac{k_1}{\theta} \leq 0, \quad \iota_2 \leq 0, \\
 & - \sum_{a=1}^{n-1} C_1^a + \frac{1}{\theta} \sum_{a=1}^{n-1} C_3^a \mu^a - \frac{k_3}{\theta} \geq 0, \quad \frac{1}{\theta} \sum_{a=1}^{n-1} C_2^a \mu^a - \frac{k_2}{\theta} - \iota_1 \geq 0, \\
 & \sum_{a=1}^{n-1} C_2^a + \iota_3 \leq 0, \quad -k_4 + \varsigma \geq 0 \quad \chi \geq 0, \\
 & \lambda + \frac{2}{3} \tau \geq 0, \quad \tau \geq 0, \quad \alpha + \frac{2}{3} \beta \geq 0, \\
 & \beta \geq 0, \quad \gamma \geq 0, \quad \varsigma \geq 0.
 \end{aligned} \tag{3.30}$$

$C_3^a$ ,  $k_1$ , and  $\iota_2$  stand for diffusion, thermal conductivity, and resistivity coefficients, respectively. In turn, phenomenological coefficients  $C_1^a$  and  $k_3$  are characteristic for the phenomenon of thermal diffusion,  $k_2$  and  $\iota_1$  for the thermoelectric phenomenon, and  $C_2^a$  and  $\iota_3$  for the electrophoretic phenomenon. All these effects are known as cross-phenomena and they present reciprocal nature, in contrast to the Fick's law, Fourier's law, and Ohm's law. Viscous properties of the electrolyte solution are accounted for by  $\lambda + 2\tau/3$ ,  $\tau$ ,  $\alpha + 2\beta/3$ ,  $\beta + \gamma$ ,  $\chi$ , and  $\varsigma$ , where  $\lambda + 2\tau/3$  and  $\tau$  denote, respectively, the bulk and shear viscosities of Newtonian fluids, while  $\alpha + 2\beta/3$ ,  $\beta$ ,  $\gamma$ ,  $\chi$ , and  $\varsigma$  are the rotational viscosities which arise due to the inner structure of the mixture.

Moreover, if one neglects all mechanisms with exception of chemical reactions in Eq. (3.29), one writes

$$\Pi = - \sum_{r=1}^R \bar{U}_r \gamma_r \geq 0, \tag{3.31}$$

which is the criterion for spontaneity of chemical reactions.

**Proposition 4** *According to the minimum conditions of the entropy production, the material parameters are subject to the constraints given in (3.30).*

#### 4 Concluding remarks

This work concerns the thermodynamics of reacting ionic mixtures. Exploiting the axiomatic nature of the constitutive theory, few expedient assumptions and, in special, the Müller–Liu entropy principle, a thermo-electrochemical continuum model is deduced for electrolyte solutions of non-volatile solutes.

The model proposed emphasizes the microscopic structure of the mixture by recognizing that internal degrees of freedom of constituent particles have an important influence on the physical and chemical properties of the mixture. Then, some elements of thermodynamics of polar fluids are incorporated to the constitutive model, and balance equations are accordingly stated.

Moreover, thermodynamic relations are obtained as natural consequences of the entropy inequality and are valid for any thermodynamic state of an electrolyte solution, either at the equilibrium or not. In addition, phenomenological equations are proposed and the conditions for the local thermodynamic equilibrium are investigated. Even though the material equations schemed are simple, they encompass a large class of physical and chemical phenomena revealed by reacting ionic mixtures.

Hence, the purpose of this work is to provide a more comprehensive and consistent approach of dynamic properties of electrolyte solutions. Once the results obtained apply for equilibrium and non-equilibrium conditions, and thermodynamic relations are not *a priori* imposed, the limitations of classical electrolyte theories are evident.

## Appendix: Expression for the Lagrange multiplier of energy $\Lambda^\varepsilon$ in an electrolyte solution

In order to show that  $\Lambda^\varepsilon = 1/\theta$  is a valid hypothesis for an aqueous electrolyte solution whose constituents are non-volatile species, one assumes that the mixture is contained in a closed vessel. In this system, the region above the solution is only filled with the vapor of the pure solvent, which is supposed to behave as an ideal gas [14]. Furthermore, the interface that separates the water vapor from the solution is regarded as a mathematical dividing plane. This assumption is suitable as long as the radius of curvature at all points of the meniscus that forms at the liquid–vapor interface is much bigger than the largest linear dimension of the meniscus. In this case, the flat solution–vapor interface may be modeled as a singular surface  $\mathcal{S}$  whose entropy jump condition is

$$[[\rho\eta(\mathbf{v} \cdot \mathbf{n} - u)]] + [[\Phi]] \cdot \mathbf{n} \geq 0. \quad (\text{A.1})$$

Moreover, as  $\mathcal{S}$  is a material surface, then  $u = \mathbf{v} \cdot \mathbf{n}$ , and Eq. (A.1) becomes

$$[[\Phi]] \cdot \mathbf{n} \geq 0. \quad (\text{A.2})$$

By making use of Eq. (A.2) and the expression of the mixture entropy flux obtained in Sect. 3.2, one has the following entropy jump condition at the electrolyte solution–solvent vapor interface

$$\left[ \Lambda^\varepsilon \mathbf{h} - \Lambda^\varepsilon \sum_{a=1}^{n-1} \mu_a \mathbf{j}_a \right] \cdot \mathbf{n} \geq 0. \quad (\text{A.3})$$

Nevertheless, as the solutes are non-volatile chemical species, then the normal components of their diffuse fluxes are null at the material surface. In addition, since the water vapor is in phase equilibrium with the solution, the entropy production at the material surface is also null [23]. Hence, Eq. (A.3) simplifies to

$$[[\Lambda^\varepsilon \mathbf{h}]] \cdot \mathbf{n} = 0. \quad (\text{A.4})$$

Because phase equilibrium causes continuity of the normal component of the heat flux at the solution–vapor interface,  $\mathbf{h} \cdot \mathbf{n}$  can be taken out of the brackets and there remains

$$[[\Lambda^\varepsilon]] = 0. \quad (\text{A.5})$$

Eq. (A.5) implies that the Lagrange multiplier of energy is the same function in both sides of the material surface, *i.e.*,  $\Lambda^\varepsilon_{\text{vapor}} = \Lambda^\varepsilon_{\text{solution}}$ . Therefore, as the Lagrange multiplier of energy for an ideal gas is proved to be  $\Lambda^\varepsilon_{\text{vapor}} = 1/\theta$  [17,24,50], it follows directly from Eq. (A.5) that  $\Lambda^\varepsilon_{\text{solution}} = 1/\theta$ . This result corroborates the choice of  $\Lambda^\varepsilon$  as the reciprocal of temperature along the constitutive modeling.

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