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Application of variational methods in chemical thermodynamics: a study of the stability of chemical systems

Martina Costa Reis[1] ·
Adalberto Bono Maurizio Sacchi Bassi[1]

Abstract The stability of chemical systems is discussed by using elementary concepts of control theory, and Lyapunov stability theory. From these concepts, a mathematically clear definition of irreversible thermodynamic processes and equilibrium states is established. Furthermore, it is shown that the extremum principles of classical thermodynamics can be obtained as natural consequences of the Lyapunov stability theory application in usual physicochemical systems. It is also demonstrated that for the case of chemical systems subject to more general physical conditions, it is possible to find a scalar function dependent of macroscopic parameters that describes the evolution of the system toward the equilibrium state. The aim of this work is to show that by using variational methods one can discuss the stability of many chemical systems.

Keywords Variational methods · Non-equilibrium thermodynamics ·
Extremum principles in thermodynamics · Dilute electrolyte solutions

1 Introduction

Together with the second law of thermodynamics, the stability of chemical systems has attracted attention of many chemists and chemical engineers along the years. By the mid-1870s, Gibbs investigated the conditions that characterize the stable states of a mixture of substances from Clausius' enunciate for the second law. In his seminal

✉ Martina Costa Reis
marreis@iqm.unicamp.br

[1] Department of Physical Chemistry, Institute of Chemistry, University of Campinas-UNICAMP, Campinas, SP, Brazil

work entitled "On the equilibrium of heterogeneous substances" [1], he introduced important concepts of chemical thermodynamics, such as chemical potential, phase rule, as well as many inequalities that later were recognized as necessary conditions for the thermodynamic stability of chemical systems at equilibrium [2,3]. In special, Gibbs also deduced necessary and sufficient conditions for the stability of homogeneous chemical systems with mass transfer in several experimental conditions.

Although Gibbs has not mentioned concepts inherent to the extremum principles in his work, one recognizes that his assertions about stability of homogeneous chemical systems are examples of application of variational methods in thermodynamics. In fact, the stability criteria laid down by Gibbs for mixtures of substances subject to adiabatic and isothermal processes are equivalent to those principles that nowadays are known as extremum principles in classical thermodynamics.

On the other hand, the stability of more complex physicochemical systems, such as supersaturated electrolyte solutions, colloidal dispersions, biochemical systems etc., cannot be studied through the classical thermodynamics approach. This occurs because in these systems there are gradients of concentration, temperature, and pressure, they may be not at rest, and the processes to which the systems are submitted are much more complex than those usually considered in classical thermodynamics. Consequently, one should use fundamental concepts of variational methods to deduce proper extremum principles to study the stability of such systems.

In this work, variational methods are employed to discuss the stability of chemical systems. In Sect. 2, basic concepts of control theory are outlined. From these concepts, a mathematically clear definition of irreversible thermodynamic processes is provided. In turn, in Sect. 3, the Lyapunov direct method [4,5] is used to find a scalar function (Lyapunov candidate function) dependent of macroscopic parameters that describes the evolution of a chemical system toward the equilibrium state. As an example, one considers a dilute electrolyte solution, which was previously studied in [6]. The Lyapunov direct method was chosen because, unlike many variational methods, it does not require the knowledge of a particular solution to study the stability of a system. From the Lyapunov candidate function, one obtains the thermodynamic conditions that characterize the equilibrium states of a dilute electrolyte solution under several physicochemical conditions.

2 Irreversibility of thermodynamic processes

Although the existence of irreversible thermodynamic processes in nature is well-accepted by everyone, the idea of irreversibility still remains as a qualitative concept. As a consequence, chemists, physicists, and engineers employ the adjectives irreversible and dissipative as synonyms to exemplify processes that involve some loss of energy not recoverable. Nonetheless, some attempts to provide a clear and mathematically coherent description of irreversible processes have been carried out since the mid-19th century, when the first statements about the second law of thermodynamics emerged [7,8]. In turn, modern mathematical descriptions of irreversible processes appeared in the second half of the twentieth century through Giles' and Willems' works [9–11].

The approach employed by Giles rests on a scale of irreversibility whereby one compares the values of an irreversibility function for different processes. His arguments are based on set theory and topology, as well as experimental evidences. On the other hand, Willems' approach stems from the foundations of control theory, an interdisciplinary mathematical theory that deals with the behavior of physical systems through the notion of *inputs* (causes, perturbations) and *outputs* (effects, responses). According to it, a system Ω is regarded as an abstract object endowed with a mathematical structure that maps *inputs* into *outputs* through a set of variables. Because in this approach physical and chemical arguments are used only when one desires to particularize the obtained results, it is more general than the approach proposed by Giles. Therefore, in this manuscript, the discussion about irreversibility of thermodynamic processes will follow from Willems' ideas.

In order to determine the conditions that result in the stability of a system in a given environment, Willems proposed an inequality that allows to identify whether a process is irreversible or not. For this purpose, he assumed that the past and current responses of the system cannot be affected by future events, as expected in all experiments. Moreover, he still supposed that the current state summarizes all past *inputs* applied on the system. Incidentally, for future responses, it does not matter how the system was brought into the current state. Once these constraints have been imposed on the system, one can consider the below definition of irreversible processes. However, to motivate the discussion about the irreversible nature of a thermodynamic process, initially some basic, but very relevant remarks are outlined.

Firstly, in this manuscript, attention is focused on systems whose dynamics is given by a set of differential equations of type

$$\frac{dx}{dt} = f(x(t), u(t)), \quad y = g(x(t), u(t)), \tag{1}$$

where $x(t)$ is an arbitrary property of the system, $u(t)$ is the input control, $y(t)$ is the output control, and $f(x, u)$ and $g(x, u)$ are smooth functions. At equilibrium, whenever $u(t^*) = 0$, such that $f(x^*, 0) = 0$ and $g(x^*, 0) = 0$, then $x(t^*) = x^*$. Such a condition characterizes the equilibrium state of the system.

Moreover, by complying with the non-equilibrium thermodynamics approach, the systems of interest are treated as continuous bodies whose properties are continuous functions of space coordinates and time. Accordingly, all dynamic equations are locally formulated, that is, the dynamic equations are given in terms of parameters that refer to a single point in space at a given time t. This approach contrasts with that employed by classical thermodynamics because in the latter physicochemical variables are independent of the space coordinates and time.

Definition 1 *Equilibrium state*. Consider a system Ω. A state $\chi(t) = (\Gamma_1(t), \ldots, \Gamma_n(t))$ of Ω is a n-tuple of time-dependent functions locally defined over Ω. In addition, in the equilibrium state $\chi(t^*) = \chi^*$, Ω is at rest in relation to the inertial reference frame κ, and the functions $\Gamma(t)$ are uniform fields over Ω. Further constraints can be also imposed in the equilibrium state by depending on the macroscopic characteristics of Ω e.g. chemical equilibrium.

Definition 2 *Macroscopic extensive properties*. The macroscopic extensive properties of Ω are given by integrals of type

$$\Psi(\chi(t)) = \int_{\mathcal{V}} \rho(\cdot, t)\psi(\cdot, t)dv, \quad \Upsilon(\chi(t)) = \int_{\partial\mathcal{V}} \phi(\cdot, t)da, \tag{2}$$

where $\mathcal{V}$ is a material region occupied by Ω in the three-dimensional Euclidean space $\mathcal{E}$ with respect to some reference configuration κ, $\partial\mathcal{V}$ is the boundary of Ω, $\rho(\cdot, t)$ is the mass density defined at a point belonging to Ω, $\psi(\cdot, t)$ and $\phi(\cdot, t)$ are quantities locally defined, and dv and da are the elements of volume and area, respectively. Besides, $\psi(\cdot, t)$ is a density *per* unit mass of Ω, and $\phi(\cdot, t)$ is a flux density *per* unit surface area of Ω, whence $\Psi(\chi(t))$ denotes a macroscopic volume quantity of Ω at the time t, as well as $\Upsilon(\chi(t))$ denotes a macroscopic surface quantity of Ω at the time t.

Definition 3 *Irreversible process*. Let $\chi(t)$ be the state of a system at the time t. Assume also that the system is submitted to a thermodynamic process. This process is irreversible in relation to the supply rate $\mathcal{W}(\chi(t), u(t), y(t))$, whenever the dissipation inequality is satisfied,

$$\mathcal{Q}(\chi(t)) - \mathcal{Q}(\chi(t_0)) \leq \int_{t_0}^{t} \mathcal{W}(\chi(t), u(t), y(t))dt, \tag{3}$$

where $\mathcal{Q}(\chi(t))$ is a non-negative function called storage function of Ω, and the integral of the supply rate on the interval $[t_0, t]$ accounts for the minimum supply necessary to bring Ω from an initial state $\chi(t_0)$ to a final state $\chi(t)$ in the most efficient way. Otherwise, a thermodynamic process is lossless or conservative in relation to the supply rate $\mathcal{W}(\chi(t), u(t), y(t))$, if the following equality

$$\mathcal{Q}(\chi(t)) - \mathcal{Q}(\chi(t_0)) = \int_{t_0}^{t} \mathcal{W}(\chi(t), u(t), y(t))dt \tag{4}$$

holds.

Hitherto, the discussion about irreversibility of a thermodynamic process is quite general. However, one may use certain properties of the system to render $\mathcal{Q}(\chi(t))$ and $\mathcal{W}(\chi(t))$ well-determined physical meanings. For example, one may particularize the discussion for physicochemical systems whose supply rate includes only a mechanical power $w(t)$, and a heat power $q(t)$. Thus, from Eq. (4), one formulates the first law of thermodynamics as

$$U(\chi(t)) - U(\chi(t_0)) = \int_{t_0}^{t} (w(t) + q(t))dt, \tag{5}$$

where $U(\chi(t))$ is the internal energy, such that $\mathcal{Q}(\chi(t)) = U(\chi(t))$, and $\mathcal{W}(\chi(t)) = w(t) + q(t)$. Note that, according to inequality (3), a process cannot be considered

irreversible in relation to $\mathcal{W}(\chi(t)) = w(t) + q(t)$. Then, in this manuscript, the concept of irreversibility rests on the considered kind of supply rate.

In turn, for the second law of thermodynamics, one needs more information because the storage function and the supply rate depend on the macroscopic characteristics of system, as well as the kind of process to which the system is submitted. For example, consider an isolated physicochemical system, which is submitted to an irreversible process. Suppose also that the system is at rest. For this system, the storage function should be identified as the entropy $S(\chi(t))$. However, while $\mathcal{Q}(\chi(t))$ is a lower bounded function, the entropy function $S(\chi(t))$ is a bounded function, so that the association between $\mathcal{Q}(\chi(t))$ and $S(\chi(t))$ is not straightforward. In order to clarify this aspect, one should recall that, according to the third law of thermodynamics, the entropy function attains its minimum value nearby the absolute zero. Indeed, by complying with the principle of maximum entropy, the entropy function should assume its maximum value at equilibrium. Conjointly, both the third law of thermodynamics and the principle of maximum entropy bound the set of values of $S(\chi(t))$ of an isolated physicochemical system at rest.

Then, if one uses the mathematical properties of exponentially bounded positive-semidefinite functions, for an isolated system, the functions $\mathcal{Q}(\chi(t))$ and $\mathcal{W}(t)$ can be respectively related to $S(\chi(t))$ and $q(t)/\theta$ by the transformations

$$S(\chi(t)) = c \exp(-\mathcal{Q}(\chi(t))), \quad \int_{t_0}^{t} \frac{q(t)}{\theta} dt = c \exp\left(-\int_{t_0}^{t} \mathcal{W}(t) dt\right), \qquad (6)$$

where c is a positive constant, and θ is the absolute temperature. Hence, with Eq. (6), inequality (3) results in

$$S(\chi(t)) - S(\chi(t_0)) \geq \int_{t_0}^{t} \frac{q}{\theta}(t) dt, \qquad (7)$$

which is the mathematical statement of the second law of thermodynamics for an isolated physicochemical system at rest. However, note that for systems subject to other physicochemical restrictions, Eq. (6) is no longer valid, and different expressions relating storage functions and supply rates to thermodynamic quantities should be found.

Furthermore, it should be emphasized that the use of transformations as shown in Eq. (6) is very common in thermodynamics. In introducing Kelvin's second absolute scale of temperature, Truesdell [7] made use of a similar procedure to obtain a scale of temperature independent of the kind of thermometric material, without ever mentioning the existence of an ideal gas. For this purpose, he used the mathematical properties of exponentially bounded positive-semidefinite functions, and later he demonstrated that Kelvin's second absolute scale of temperature is definitely coherent with Clausius' and Kelvin's works [12,13] published in 1853. Indeed, the exploitation of mathematical properties of an exponentially bounded positive-semidefinite function is somewhat recurrent in quantum mechanics [14].

3 Lyapunov functions and stability of chemical systems

This section presents the stability criteria of an equilibrium state based on the concept of distance function. Besides, it also exploits the Lyapunov direct method to predict the stability of an equilibrium state of a dilute electrolyte solution.

3.1 Notions of stability implied by the Lyapunov theorem

Let a chemical system be in the equilibrium state occurring till an instant previous to $t = 0$, say $t_{-1} < 0$. Suddenly, at t_{-1} the system experiences a change of concentration, temperature, or pressure due to external sources, and then it leaves its equilibrium state. However, as soon as the initial external conditions are restored at $t = 0$ and maintained at all future times $t > 0$, one can ask whether the chemical system will return to its original equilibrium state. For example, one may admit that after a sufficiently small perturbation, the states reached by the system will stay nearby the original equilibrium state at all later times. Indeed, one may also consider that besides staying in the neighborhood of χ^*, such perturbed states will eventually tend to the original equilibrium state as time goes to infinity.

These hypotheses are physically well-motivated if one considers, for instance, the motion of a simple gravity pendulum: one may impose a perturbation to a pendulum originally at equilibrium, so that it starts oscillating with an amplitude ω. Then, if one describes the motion of the pendulum by an idealized mathematical model, that is, a weight on the end of a massless cord suspended by a pivot and subject to no air drag and friction, the pendulum indefinitely oscillates with constant amplitude. But, if one considers the dynamics of a real pendulum, that is, a weight on the end of a cord with mass m suspended by a pivot and subject to air drag and friction, the oscillation certainly declines as time goes, and the original equilibrium state is asymptotically reached as time tends to infinity.

Mathematically, the stability criteria described above can be put in a more elegant way by defining a metric for the thermodynamic state space [15,16]. For this purpose, one needs to introduce (i) a proper distance function d that defines the distance between two distinct states $\chi_1(t)$ and $\chi_2(t)$ belonging to the thermodynamic state space, (ii) the class of perturbations that will be considered in such space, and (iii) the existence of a function that indicates the system time evolution toward stability.

Definition 4 *Stable state*. An equilibrium state χ^* is stable, if for every $\tau > 0$ there exists $\delta > 0$, such that for the state χ_0 occurring at time $t = 0$, the inequality

$$d(\chi_0, \chi^*) < \delta \tag{8}$$

implies

$$d(\chi(t), \chi^*) < \tau \quad \forall t \geq 0. \tag{9}$$

In other terms, the above inequalities mean that an equilibrium state is stable, if there exists an upper bounded set of disturbances, such that by restoring the initial external
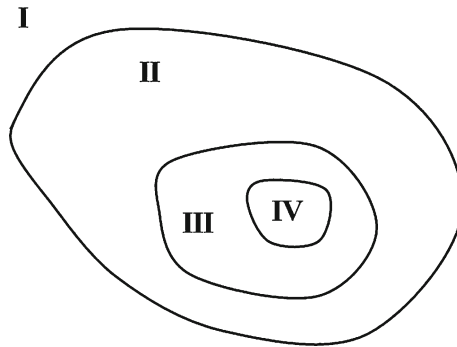
Fig. 1 Universe of all possible states of a system. Region *I* includes non-equilibrium states, and region *II* includes those equilibrium states where Definitions 4 and 5 do not apply. In turn, the region *III* represents the stable states where Definition 5 does not apply, and finally region *IV* represents the asymptotically stable states. The union of regions *I*, *II*, *III*, and *IV* comprises the set of all possible states of a system submitted to an irreversible process. Similarly, the union of regions *II*, *III*, and *IV* is the set of all possible equilibrium states, as well as the union of regions *III* and *IV* constitutes the set of all possible stable states

conditions the current state of system remains close to the τ-neighborhood of the state χ^* at all future times.

Definition 5 *Asymptotically stable state*. An equilibrium state χ^* is asymptotically stable, if χ^* is stable in the sense of Definition 4, and there exists $\tilde{\delta} > 0$, such that the inequality

$$d(\chi_0, \chi^*) \leq \tilde{\delta} \tag{10}$$

implies

$$d(\chi(t), \chi^*) \to 0 \quad t \to \infty. \tag{11}$$

Incidentally, the equilibrium state is said to be asymptotically stable, if it is stable, and there exists an upper limited set of disturbances, so that by restoring the initial external conditions the state of system converges to χ^* as time tends to infinity.

Thus, according to the above definitions, every stable state is an equilibrium state. Analogously, every asymptotically stable state is stable in the sense of Definition 4, and also is an equilibrium state (Fig. 1). Nevertheless, from the practical point of view, only the asymptotically stable states are thermodynamically relevant as the equilibrium state is never rigorously reached. As a matter of fact, in thermodynamics one says that a system reaches the equilibrium state, when changes in macroscopic parameters can no longer be observed by the available measuring devices.

The definitions about the stable and asymptotically stable states of a physicochemical system tell us nothing about what happens during the temporal evolution of system toward its stability. However, if the Lyapunov direct method is used, one can obtain some conclusions about the system evolution in the direction to equilibrium state, although the process that brings the system from $\chi(t)$ to χ^* is not known.

Definition 6 *Lyapunov candidate function*. Suppose that a system submitted to an irreversible process possesses a stable state χ^*. A scalar-valued function $\mathcal{L}(\chi(t))$ is a Lyapunov candidate function, if for every attainable irreversible process it holds the following properties:

1. $\mathcal{L}(\chi(t))$ is a monotonically non-increasing function of time on a neighborhood of χ^*;
2. $\mathcal{L}(\chi(t))$ is a continuous function at χ^*;
3. $\mathcal{L}(\chi(t))$ has a strong local minimum at χ^*. In other terms, χ^* is a strong local minimum of $\mathcal{L}(\chi(t))$, if

$$\mathcal{L}(\chi(t^*)) < \mathcal{L}(\chi(t)) \quad \forall \chi(t) \in \mathcal{N}(\chi(t^*), \tau),$$

where $\mathcal{N}(\chi(t^*), \tau)$ is the set of feasible points contained within the τ-neighborhood of $\chi(t^*)$.

As a consequence of Definition 6, on the τ-neighborhood of χ^* the Lyapunov candidate functions obey the inequality

$$\frac{d}{dt}\mathcal{L}(\chi(t)) \leq 0. \tag{12}$$

In fact, Lyapunov candidate functions are of great relevance for stability problems because from the time derivative of $\mathcal{L}(\chi(t))$ it is possible to test the stability of an equilibrium state, according to the Lyapunov theorem [17]. Although the proof of this theorem is omitted here because it can be easily found in several mathematical references (for example, see [4,5,18]), its physical implications are presented. Nonetheless, prior note that by considering $\mathcal{Q}(\chi(t))$ sufficiently smooth, inequality (3) may be rewritten as

$$\frac{d}{dt}\mathcal{Q}(\chi(t)) \leq \mathcal{W}(\chi(t), u(t), y(t)). \tag{13}$$

Thus, whenever the supply rate is not positive in a sufficiently small neighborhood of a stable state, the dissipation inequality is the Lyapunov inequality [expression (12)], which can be regarded as a particular case of the former.

Theorem 1 *Lyapunov theorem. Let χ^* be a stable state of a system submitted to an irreversible process. In the τ-neighborhood of χ^*, the system storage function is a Lyapunov candidate function that satisfies inequality (12). An equilibrium state is said to be stable, if $d\mathcal{L}(\chi(t))/dt$ is negative semi-definite. In turn, an equilibrium state is said to be asymptotically stable, if $d\mathcal{L}(\chi(t))/dt$ is negative definite.*

Usually, the Lyapunov candidate functions contain great physical significance. For example, for a closed system at rest submitted to an adiabatic process, the Lyapunov candidate function is symmetric to the logarithm of a monotonically non-decreasing

function named entropy $S(t)$. This function attains its strong local maximum at the stable state, namely

$$\frac{d}{dt}S(t) \geq 0. \tag{14}$$

In turn, for a closed system at rest submitted to an isothermal process, the Lyapunov candidate function is given by a monotonically non-increasing function named Helmholtz energy $A(t)$. This function attains its strong local minimum at the stable state, viz.

$$\frac{d}{dt}A(t) \leq 0. \tag{15}$$

Moreover, note that inequalities (14) and (15) are the mathematical statements of two well-known extremum principles in thermodynamics. Such principles and their equivalent forms are used in thermodynamics to prove the stability of physicochemical systems. In the next section, the Lyapunov direct method will be used to find the thermodynamic conditions that ensure the stability of an equilibrium state of a dilute electrolyte solution under several physicochemical conditions.

3.2 Stability of the equilibrium state of dilute electrolyte solutions

In order to study the stability of the equilibrium state of dilute electrolyte solutions, one starts considering the governing dynamic equations of electrolyte solutions. These equations were comprehensively discussed by Reis and Bassi [19]. Therefore, they will be briefly outlined here.

Balance of mass concentration

$$\frac{d}{dt}\int_{\mathcal{V}} \rho\xi_a dv - \int_{\partial\mathcal{V}} \mathbf{j}_a \cdot \mathbf{n}da - \int_{\mathcal{V}} c_a dv = 0 \quad a = 1, \ldots, n-1, \tag{16}$$

Balance of linear momentum

$$\frac{d}{dt}\int_{\mathcal{V}} \rho\mathbf{v}dv - \int_{\partial\mathcal{V}} \mathbf{t}da - \int_{\mathcal{V}} \rho\mathbf{b}dv = \mathbf{0}, \tag{17}$$

Balance of angular momentum

$$\frac{d}{dt}\int_{\mathcal{V}} \mathbf{o} \wedge \rho\mathbf{v}dv - \int_{\partial\mathcal{V}} \mathbf{o} \wedge \mathbf{t}da - \int_{\mathcal{V}} \mathbf{o} \wedge \rho\mathbf{b}dv = \mathbf{0}, \tag{18}$$

Balance of energy

$$\frac{d}{dt}\int_{\mathcal{V}} \left(\rho\varepsilon + \frac{1}{2}\rho\mathbf{v} \cdot \mathbf{v}\right) dv - \int_{\partial\mathcal{V}} (\mathbf{v} \cdot \mathbf{t} - \mathbf{h} \cdot \mathbf{n})da - \int_{\mathcal{V}} (\rho\mathbf{b} \cdot \mathbf{v} + \rho r)dv = 0, \tag{19}$$

Balance of entropy

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \eta \, dv + \int_{\partial \mathcal{V}} \boldsymbol{\Phi} \cdot \mathbf{n} \, da - \int_{\mathcal{V}} \rho \sigma \, dv \geq 0, \tag{20}$$

where ξ_a is the mass concentration of a constituent a of the solution, being the index n reserved for the solvent, $\mathbf{j}_a$ is the diffusive flux of a constituent a, $\mathbf{n}$ is the outward unit normal vector to the boundary $\partial \mathcal{V}$, c_a is the mass production of a constituent a due to chemical reactions, $\mathbf{v}$ is the barycentric velocity of the solution, $\mathbf{t}$ is the surface traction that is related to the stress tensor $\boldsymbol{T}$ by $\mathbf{t} = \boldsymbol{T} \mathbf{n}$, $\mathbf{b}$ is the body force, $\mathbf{o}$ is the position vector with respect to the mass center of the solution, ε is the local internal energy density, $\mathbf{h}$ is the heat flux vector, r is the energy source, η is the local entropy density, $\boldsymbol{\Phi}$ is the entropy flux vector, and σ is the entropy source.

Here, it was assumed that the angular momentum of solution is conserved, and the solution is so diluted that its dynamics is given by the dynamics of the solvent. Thus, only one balance equation of linear momentum, and one balance equation of internal energy, both valid for the whole solution, are employed. Moreover, by complying with Truesdell's axiom of dissipation [20], the entropy production of each constituent of solution may assume positive, negative or even null values, as long as the entropy production of solution as a whole is non-negative.

To find the Lyapunov candidate function that describes the time evolution of a dilute electrolyte solution toward the equilibrium state, one uses Eqs. (16)–(20) to obtain the macroscopic extensive properties (see Definition 2), and the fact that the entropy flux vector is given by $\boldsymbol{\Phi} = \mathbf{h}/\theta - \sum_{a=1}^{n-1} \mu_a \mathbf{j}_a / \theta$, where μ_a is the chemical potential of a constituent a [6]. In addition, one assumes that the surface traction is associated to the hydrostatic pressure by $\mathbf{t} = -p\mathbf{n}$. With these assumptions, one subtracts the balances of energy and mass concentration from the balance of entropy in order to eliminate the contributions of the heat and diffusive fluxes on the entropy flux. Then, the resulting expression is

$$\frac{d}{dt} \int_{\mathcal{V}} \left(\rho \varepsilon + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} - \theta \rho \eta + \sum_{a=1}^{n-1} \rho \xi_a \mu_a \right) dv + \int_{\partial \mathcal{V}} (\mathbf{v} \cdot p\mathbf{n}) \, da - \int_{\mathcal{V}} \sum_{a=1}^{n-1} c_a \mu_a \, dv \leq 0. \tag{21}$$

Expression (21) may be further simplified if one initially recalls the theorem of transport [21], theorem of divergence, and assumes that the motion of the solution is isochoric, *viz.*

$$\frac{d}{dt} \int_{\mathcal{V}} dv = \int_{\mathcal{V}} \operatorname{div}(\mathbf{v}) = \int_{\partial \mathcal{V}} \mathbf{v} \cdot \mathbf{n} \, da, \quad V(t) = \int_{\mathcal{V}} dv. \tag{22}$$

Thus, by multiplying expression (22) by $-p$ and subtracting it from expression (21), the latter becomes

$$\frac{d}{dt} \int_{\mathcal{V}} \left(\rho \varepsilon + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} - \theta \rho \eta + \sum_{a=1}^{n-1} \rho \xi_a \mu_a + p \right) dv - \int_{\mathcal{V}} \sum_{a=1}^{n-1} c_a \mu_a \, dv \leq 0, \tag{23}$$

or yet,

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \left(\varepsilon + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} - \theta \eta + \sum_{a=1}^{n-1} \xi_a \mu_a + \frac{p}{\rho} \right) dv - \int_{\mathcal{V}} \sum_{r=1}^{R} \eth_r \Lambda_r dv \leq 0, \quad (24)$$

where $\sum_{a=1}^{n-1} c_a \mu_a = \sum_{r=1}^{R} \eth_r \Lambda_r$ was used, such that $\eth_r$ is symmetric to the chemical affinity of a reaction r, and Λ_r is the rate of conversion of r by supposing R independent chemical reactions.

Chemical equilibrium

The discussion about the stability of a dilute electrolyte solution proceeds by imposing that chemical equilibrium has been reached at all points of the solution. Hence, $\int_{\mathcal{V}} \sum_{r=1}^{R} \eth_r \Lambda_r dv = 0$, and Eq. (24) becomes

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \left(\varepsilon + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} - \theta \eta + \sum_{a=1}^{n-1} \xi_a \mu_a + \frac{p}{\rho} \right) dv \leq 0, \quad (25)$$

whence the Lyapunov candidate function is given by

$$\mathcal{L}(t) = \int_{\mathcal{V}} \rho \left(\varepsilon + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} - \theta \eta + \sum_{a=1}^{n-1} \xi_a \mu_a + \frac{p}{\rho} \right) dv, \quad \frac{d}{dt} \mathcal{L}(t) \leq 0. \quad (26)$$

In this case, $\mathcal{L}(t)$ can be understood as a function that includes contributions arising from the barycentric motion of the solution, mass concentration, temperature, and pressure. Moreover, this Lyapunov candidate function is also valid for the case of a non-reactive dilute electrolyte solution.

Solution at rest and chemical equilibrium

One specializes the above results for the case of a dilute electrolyte solution that is at rest in relation to an inertial reference, and all chemical reactions are at chemical equilibrium. With such constraints, Eq. (24) comes to

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \left(\varepsilon - \theta \eta + \sum_{a=1}^{n-1} \xi_a \mu_a + \frac{p}{\rho} \right) dv \leq 0, \quad (27)$$

whence the Lyapunov candidate function is

$$\mathcal{L}(t) = \int_{\mathcal{V}} \rho \left(\varepsilon - \theta \eta + \sum_{a=1}^{n-1} \xi_a \mu_a + \frac{p}{\rho} \right) dv, \quad \frac{d}{dt} \mathcal{L}(t) \leq 0. \quad (28)$$

Here, unlike the previous case, the Lyapunov candidate function includes only contributions related to the mass concentrations of constituents of the solution, temperature, and pressure.

Homogeneous solution at rest and chemical equilibrium

In this particularization, one imposes further constraints on the solution. The dilute electrolyte solution remains at rest in relation to an inertial reference and all chemical reactions are at chemical equilibrium. However, now the solution is homogeneous in relation to the mass concentration (absence of diffusive fluxes) of all constituents. In order to clarify this point, one recalls Eq. (16). By imposing absence of diffusive fluxes, one obtains

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \xi_a dv - \int_{\mathcal{V}} c_a dv = 0 \quad a = 1, \ldots, n-1, \tag{29}$$

according to which all changes in ξ_a are exclusively due to chemical reactions. But, if chemical equilibrium is also imposed, then $\int_{\mathcal{V}} c_a dv = 0$, and Eq. (29) turns into

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \xi_a dv = 0 \quad a = 1, \ldots, n-1, \tag{30}$$

whence one notices that the mass concentration of a constituent a remains constant. However, note that, according to Eq. (16), the imposition of chemical equilibrium with presence of diffusive fluxes is not sufficient to ensure Eq. (30). Besides, observe that, in general, the imposition of chemical equilibrium together with absence of diffusive fluxes usually leads to the homogeneity of solution with respect to the mass concentration of the constituents, temperature, pressure, and other parameters that affect the equilibrium constant of a reaction. Under such circumstances, the solution presents a uniform temperature $\hat{\theta}$ and pressure $\hat{p}$, and the equilibrium constant is homogeneous. As a matter of fact, such a picture is similar to that employed in classical thermodynamics to represent chemical systems.

Therefore, in view of the above considerations, it follows from Eq. (24) that

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \left(\varepsilon - \hat{\theta} \eta + \frac{\hat{p}}{\rho} \right) dv \leq 0. \tag{31}$$

Equation (31) is an equivalent form of the principle of minimum energy for homogeneous chemical systems at rest and at chemical equilibrium. As usual, the Lyapunov candidate function for this case is the Gibbs energy, viz.

$$\mathcal{L}(t) = \int_{\mathcal{V}} \rho \left(\varepsilon - \hat{\theta} \eta + \frac{\hat{p}}{\rho} \right) dv, \quad \frac{d}{dt} \mathcal{L}(t) \leq 0, \tag{32}$$

which fully characterizes the behavior of solution in equilibrium over a wide range of temperature, and pressure.

4 Concluding remarks

In this work, variational methods are used to discuss the stability of physicochemical systems, particularly dilute electrolyte solutions. By imposing several constraints

on these solutions, one obtains different scalar-valued functions dependent of macroscopic parameters that describe the evolution of the system toward its stability. Indeed, it was demonstrated that only when one imposes the homogeneity of the solution in relation to the mass concentration of all constituents, mechanical rest, and chemical equilibrium, the stability of dilute electrolyte solutions may be described by the Gibbs energy. On the other hand, for all other cases, one can obtain Lyapunov candidate functions not classically defined, but that tend to a strong local extremum. This shows that stability criteria of classical thermodynamics cannot be uncritically used to study the stability of chemical systems.

Although the Lyapunov direct method does not provide information about the process used by the system to reach the equilibrium state, the method is very useful as it allows to understand what happens with the system during the process. Furthermore, the wide scope of the Lyapunov direct method allows that the stability of any chemical system is studied. As a matter of fact, the study of stability of dilute electrolyte solutions in this manuscript is a simple example of how Lyapunov direct method is important to discuss the stability of chemical systems in physicochemical conditions where the methods of classical thermodynamics are not applicable.

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