

The Thermodynamic Characterization of Spontaneous Electrochemical Reactions

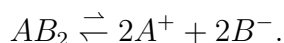
Joseph W. Jerome^{a,*}

^aMathematics Department, Northwestern University,
Evanston, IL 60208-2730, USA

We consider whether the association of charged species of opposite parity in a chemical cell constitutes a spontaneous reaction. The initial distributions of the species are modeled as a steady-state phenomenon, characterized by a drift-diffusion system and two coupled constraints: (1) the electroneutrality of net system charge; and, (2) a coupled thermodynamic inequality constraint, reflecting the net decrease of the Gibbs' free energy in the closed system required for any spontaneous chemical reaction leading to uniform association of the species. A useful analytical technique of partial convexity allows the reformulation of thermodynamic compatibility. A control theory interpretation of the Dirichlet boundary conditions allows the selection of a trapping region for the range of the solution components which ensures that the reaction is spontaneous. A specific application is the production of hydrogen in an electrochemical cell. This is contained in a larger modeling context: reduction processes in electrochemistry. The final section describes extensions of the modeling in which an open mathematical problem and a pointer to the nonisothermal case are identified.

1. Introduction

We consider isothermal chemical reactions at a fixed temperature $T > 0$ of the form,



We will consider only the reverse reaction of association, which is motivated by the oxidation-reduction processes of electrochemical cells. For these reactions, we assume the stoichiometry is such that for each mole of the cation A^+ and each mole of the anion B^- , one-half mole of the product forms. Routine modifications of the stoichiometry are possible to include other reduction processes. Our analysis is motivated by, but not restricted to, the second stage of a two-stage process occurring in a modern fuel cell with semiconductor electrodes. For fuller physical descriptions, we refer the reader to [1–3]. The first stage, examined mathematically in [4], involves illumination of the electrodes, releasing electrons and holes into solution under thermodynamic compatibility with oxygen and hydrogen evolution. Anodic oxidation of water occurs, in which the holes are

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transformed into hydrogen ions (protons). The second stage (reduction) involves the association of hydrogen ions and electrons to form hydrogen. In the notation above, H_2 is identified with the product AB_2 . It is this type of reaction which we study with respect to chemical spontaneity. In the terminology of electrochemistry, it is a half-cell reaction with a specified right electrode, with the cell completed by a reference electrode (left electrode). Spontaneity has a technical meaning in electrochemistry: the change ΔG of the Gibbs free energy of the closed system is nonpositive. This is equivalent to the statement that the change ΔS in the entropy of the universe is nonnegative, provided only energy (but not matter) is exchanged with the outside of the system. We make the simplifying assumption that the electrolyte is an ideal solution. This means that we are not directly incorporating the Debye-Hückel theory, and that we assume the effective concentrations are equal to the actual concentrations. In the final section, we concisely describe a model incorporating the Debye-Hückel theory, and pose an open problem. In this paper, well-posedness is established only for ideal solutions. In our formulation, we shall use what physical chemists call the (partial) electrochemical potential μ_C , associated with a given species C , so that the Gibbs free energy density prior to the reaction is characterized by

$$\mathcal{G}_r = \sum_{\text{reactants}} \mu_C N_C,$$

where N_C is the molar density of C (see [5, p. 524]), and the free energy after the reaction by

$$\mathcal{G}_p = \sum_{\text{products}} \mu_C N_C.$$

Thus, we are defining a model based on macroscopic, rather than microscopic, principles. The stoichiometry specifies the number of times a term appears in each summation. The criterion of a spontaneous reaction is obtained by integration of the density:

$$\Delta G = \int_{\Omega} \{\mathcal{G}_p - \mathcal{G}_r\} dx \leq 0,$$

where Ω denotes the physical region occupied by the electrolyte solution.

1.1. Criteria for the Associative Reaction

For an ideal solution, we have the following definition of μ_C [6, pp. 134,150]:

$$\mu_C = \mu_C^0 + RT \ln N_C + zFu, \tag{1}$$

where F is the Faraday constant, $z = -1, 0, 1$, and R is the universal gas constant. The values of z correspond to anion, neutral, and cation species, respectively. μ_C^0 is an equilibrium value tabulated in the physical chemistry literature for a broad class of reactions and N_C is the concentration relative to the standard state (moles per liter). For the reactants, we shall identify C with either A^+ or B^- and designate by p and n the non-constant molar concentration densities of A^+ cations and B^- anions, respectively. We designate by the constant M the product concentration of AB_2 at equilibrium, to be completely specified in due course, and by M_0 its integral over Ω . In particular, we have the representations

$$\mathcal{G}_r = 2p\mu_{A^+} + 2n\mu_{B^-}, \quad \mathcal{G}_p = M\mu_{AB_2}. \tag{2}$$

Units are chosen so that $\frac{RT}{F} = 1$, and potentials v and w via

$$n = N_0 \exp(u - v), \quad p = P_0 \exp(w - u). \quad (3)$$

The electroneutrality principle requires that the concentrations satisfy

$$\int_{\Omega} n \, dx = 2M_0 = \int_{\Omega} p \, dx, \quad (4)$$

which fixes N_0, P_0 . This represents one of the two constraints on the system. These relations, the definition (1), and the characterization (2), provide the second constraint. In fact, the criterion $\Delta G \leq 0$ is expressed:

$$0 \geq -C^0/F + 2 \int_{\Omega} (nv - pw) \, dx + M_0(\ln M - 2 \ln P_0 - 2 \ln N_0). \quad (5)$$

The (assumed positive) number,

$$C^0/F = (2M_0)(\mu_{A^+}^0 + \mu_{B^-}^0 - \frac{1}{2}\mu_{AB_2}^0)$$

represents the reaction at standard conditions, given the specified electrodes. We elaborate [7]. Given the cell emf E , defined as the difference between right and left hand electrode potentials at standard conditions, C^0 can be expressed [7, pp. 86,93] as

$$C^0/F = 2M_0E = 2M_0(v_0 - w_0), \quad (6)$$

where v_0 is tabulated and $w_0 < v_0$ is the given left-hand electrode potential. In a given application, w_0 might be specified by oxygen evolution. We shall employ two normalizations in the sequel: $M = 1$ (so that the product concentration is one mole per liter) and $|\Omega| = 1$ so that $M_0 = 1$. These are for convenience only, and do not affect the analytical results.

1.2. The Boundary Value Formulation

The system presented here is a standard drift-diffusion system corresponding to charge induced by two species of opposite parity: cations and anions. We retain the definitions of u, n, p presented in the previous subsection. The isothermal model, prior to association, is presented as:

$$-\nabla \cdot [\epsilon \nabla u] + n - p = 0, \quad (7)$$

$$-\nabla \cdot [\mu_n n \nabla u - D_n \nabla n] = 0, \quad (8)$$

$$-\nabla \cdot [\mu_p p \nabla u + D_p \nabla p] = 0. \quad (9)$$

The dielectric satisfies $\epsilon(x) \geq \epsilon_0 > 0$, and is an L_{∞} function of the position x only. Similar considerations apply to the mobility and diffusion coefficients, and we employ the Einstein relations; the thermal voltage RT/F is 1 in our units. The system is augmented by boundary conditions of mixed type, including homogeneous Neumann boundary conditions on $\Gamma \subset \partial\Omega$ and equilibrium Dirichlet boundary conditions on the contact portions

(electrodes) $\partial\Omega \setminus \Gamma$. In terms of the electrochemical potentials v and w , the system (7), (8), and (9) is rewritten as

$$-\nabla \cdot [\epsilon \nabla u] + N_0 e^{u-v} - P_0 e^{w-u} = 0, \quad (10)$$

$$-\nabla \cdot [\mu_n e^{u-v} \nabla v] = 0, \quad (11)$$

$$-\nabla \cdot [\mu_p e^{w-u} \nabla w] = 0. \quad (12)$$

The solutions of this system are required to satisfy (4, 5, 6), with $M = M_0 = 1$ and Dirichlet boundary conditions on the left electrode Σ_1 and the right electrode Σ_2 . We write these as

$$u = v = w = \sigma_1 \text{ on } \Sigma_1, \quad u = v = w = \sigma_2 \text{ on } \Sigma_2.$$

The appropriate way to see this is through the interpretation of σ_1, σ_2 as control variables. This applies specifically to the electrostatic potential u , since equilibrium boundary conditions then give $u = v = w$ on each of the two electrodes defining $\partial\Omega \setminus \Gamma$. In effect, we raise the left electrode potential and lower the right electrode potential with respect to standard conditions. This is directly related to the trapping region for the solutions. The extreme example of this is now briefly discussed.

1.3. The Special Case of Equilibrium

Given v_0, w_0 as above, we define the equilibrium potential

$$u_0 = \frac{1}{2}(v_0 + w_0).$$

It follows that the special equilibrium solution $u = u_0, v = u_0, w = u_0$, leading to

$$n = p = 2,$$

satisfies the steady-state system above with constant Dirichlet boundary conditions $u = u_0, v = u_0, w = u_0$. The product reaction is spontaneous if $C^0 \geq 0$ in this case.

2. Mathematical Well-Posedness

The natural progression is to formulate a sufficient condition for the thermodynamic inequality. This is achieved by partial convexity. We first restate the Gibbs inequality:

$$0 \geq (w_0 - v_0) - \ln N_0 - \ln P_0 + \int_{\Omega} (nv - pw) dx. \quad (13)$$

2.1. A Partial Convexity Inequality for Thermodynamic Spontaneity

Define the function of two variables (y, z) ,

$$J(y, z) = N_0 \exp(u - y) + P_0 \exp(z - u),$$

for fixed u . The Hessian is positive definite, and J is globally convex in (y, z) . By convexity, there is a tangent plane at $[(v, w), J(v, w)]$ lying below the graph of J , such that

$$J(y, z) \geq J(v, w) + J_v(v, w)(y - v) + J_w(v, w)(z - w).$$

Here, the subscripts denote partial derivatives. The choice $(y, z) = (v_*, w_*)$ gives:

$$\begin{aligned} N_0 \exp(u - v_*) + P_0 \exp(w_* - u) &\geq N_0 \exp(u - v) + P_0 \exp(w - u) \\ &+ N_0(v - v_*) \exp(u - v) + P_0(w_* - w) \exp(w - u). \end{aligned}$$

If we select for (u, v, w) a solution triple, satisfying the electroneutrality condition, and integrate we obtain

$$0 \geq \int_{\Omega} \{(n + p) - (n_* + p_*) - nv_* + pw_*\} dx + \int_{\Omega} (nv - pw) dx.$$

Here we have defined $n_* = N_0 \exp(u - v_*)$, $p_* = P_0 \exp(w_* - u)$. We shall identify v_* , w_* with upper and lower bounds for the trapping region which bounds u, v, w . In particular, $v \leq v_*$, $w \geq w_*$, so that $n \geq n_*$, $p \geq p_*$. Comparison with the Gibbs inequality (13) then reveals that the latter is satisfied if

$$(v_0 - w_0) + \ln N_0 + \ln P_0 + 2(w_* - v_*) \geq 0. \quad (14)$$

2.2. The Trapping Region

Suppose that a solution of the system coupled to the electroneutrality constraint satisfies inequalities of the form,

$$w_* \leq u, v, w \leq v_*, \quad (15)$$

where $v_* - w_* \leq (v_0 - w_0)/4$. Then the Gibbs inequality (13) is satisfied. Indeed, we note that

$$\ln N_0 + \ln \left(\int_{\Omega} \exp(u - v) dx \right) = \ln 2, \quad \ln P_0 + \ln \left(\int_{\Omega} \exp(w - u) dx \right) = \ln 2,$$

so that

$$\max(|\ln N_0/2|, |\ln P_0/2|) \leq v_* - w_*,$$

and, hence, (14) via

$$(v_0 - w_0) + \ln N_0 + \ln P_0 + 2(w_* - v_*) \geq (v_0 - w_0) - 4(v_* - w_*) \geq 0.$$

2.3. The Main Result

We choose the Dirichlet boundary conditions $\sigma_1 = w_*$, $\sigma_2 = v_*$. We have the following result.

Theorem 2.1. *There exists a weak solution of the system (10, 11, 12) satisfying homogeneous Neumann boundary conditions weakly on Γ and the Dirichlet boundary conditions just cited on $\Sigma_1 \cup \Sigma_2 = \partial\Omega \setminus \Gamma$. This solution satisfies electroneutrality (4) and thermodynamic compatibility (13) with the normalizations $M = M_0 = 1$ and lies in the trapping region (15).*

We shall prove the theorem in the following subsections. The idea is to define a mapping T , which embeds the trapping region in its definition, and to exhibit fixed points of T , via the Schauder theorem, which define solutions.

2.4. The Mapping

In this section, we shall define the domain and action of the mapping T . The trapping region domain is designed, in accordance with a previous subsection, to induce the Gibbs inequality. The map itself will incorporate the features of the system, as well as the electroneutrality. Consider the individual mappings U, S defined as follows. The domain of U is the closed convex set in L_2 ,

$$\mathcal{D}_U = \{u \in L_2(\Omega) : w_* \leq u \leq v_*\},$$

where the pointwise inequalities are understood ‘almost everywhere’. Then $U(u) = [v, w]$ if v, w (uniquely) satisfy the weak version of the decoupled gradient system:

$$\begin{aligned} -\nabla \cdot [\mu_n e^{u-v} \nabla v] &= 0, \\ -\nabla \cdot [\mu_p e^{w-u} \nabla w] &= 0, \end{aligned}$$

subject to the following Dirichlet boundary conditions:

$$v = w = w_* \text{ on } \Sigma_1, \quad v = w = v_* \text{ on } \Sigma_2. \quad (16)$$

We will subsequently show that $[v, w] \in \mathcal{D}_S$, where

$$\mathcal{D}_S = \{[v, w] \in \prod L_2(\Omega) : w_* \leq v, w \leq v_*\}.$$

Intermediate numbers,

$$N_0 = N_0(u, v), \quad P_0 = P_0(u, w),$$

are introduced so as to guarantee electroneutrality:

$$N_0 \int_{\Omega} \exp(u - v) \, dx = 2, \quad P_0 \int_{\Omega} \exp(w - u) \, dx = 2.$$

We then define $S[v, w] = \tilde{u}$ if \tilde{u} solves the weak form of the gradient equation

$$-\nabla \cdot [\epsilon \nabla \tilde{u}] + N_0 e^{\tilde{u}-v} - P_0 e^{w-\tilde{u}} = 0,$$

subject to the specified boundary conditions on \tilde{u} . We have: $T = S \circ (N_0, P_0) \circ U$.

2.5. Properties of the Mapping and Fixed Points

Since the transformation $v \mapsto V = \exp(-v), w \mapsto W = \exp(w)$, leads to linear equations for V, W , existence of solutions $[v, w]$ with range contained in the Cartesian product

$$[w_*, v_*] \times [w_*, v_*]$$

is standard. Suppose u_1, u_2 are given in the domain of U . We give the argument, via sequential continuity, which compares V_1, V_2 , where $u_i \mapsto V_i, i = 1, 2$. The corresponding argument for W_1, W_2 is similar, and is omitted. The weak solution characterizations yield

$$\int_{\Omega} \mu_n \exp(u_1) |\nabla(V_1 - V_2)|^2 \, dx \leq \int_{\Omega} \mu_n |\exp(u_1) - \exp(u_2)| |\nabla V_2| |\nabla(V_1 - V_2)| \, dx,$$

with test function defined by $V_1 - V_2$. Note that the factor $\exp(u_1)$ cannot be less than $\exp(w_*)$. After application of the Schwarz inequality and division by $\|\nabla(V_1 - V_2)\|_2$, we consider the sequential convergence of $u_2 \rightarrow u_1$ in L_2 . A subsequence of every subsequence of $V_2 = V(u_2)$ is convergent to $V_1 = V(u_1)$ as is seen by utilizing pointwise subsequential convergence of the L_2 convergent sequence $\exp(u_2) \rightarrow \exp(u_1)$ and by making use of Lebesgue's dominated convergence theorem. This yields sequential continuity of U . The continuity of the mapping yielding (N_0, P_0) is shown to be continuous from the continuity of Carathéodory mappings composed with integration.

The existence of a weak solution of the gradient equation defining the mapping S follows the analysis of [8]. The trapping region argument requires the idea of lower and upper solution utilized in [9]; w_* is a lower solution and v_* is an upper solution. The continuity of S is established in a manner similar to [8, Lemma 4.3], with addition of an extra term required to accommodate the mapping (N_0, P_0) . Moreover, the range of T is relatively compact. The Schauder theorem yields a fixed point u in the trapping region. The electroneutrality is built into the mapping T . The trapping region is designed to imply thermodynamic compatibility. This gives the desired solution and concludes the proof.

3. Generalization: Open Problem and Extensions

We present the generalized version incorporating the Debye-Hückel theory for sufficiently dilute solutions.

3.1. The Gibbs Criterion

For a non-ideal solution, we have the following definition of μ_C [6, p. 153]:

$$\mu_C = \mu_C^0 + RT \ln(\gamma_C N_C) + zFu,$$

where, again, F is the Faraday constant, $z = -1, 0, 1$, and R is the universal gas constant. The γ_C are termed the activity coefficients. As is typical, we represent the sum (average) of these coefficients via the Debye-Hückel theory for sufficiently dilute solutions [6, p. 156–159]:

$$\ln \gamma_{A^+} + \ln \gamma_{B^-} = -\alpha\sqrt{I},$$

for a constant α depending on temperature, where I is the ionic strength, given here as

$$I = \frac{1}{2}(n + p).$$

The reformulation of $\Delta G \leq 0$ now becomes (with the normalizations chosen earlier):

$$0 \geq -C^0/F + 2 \int_{\Omega} (nv - pw) dx - 2 \ln P_0 - 2 \ln N_0 + \sqrt{2}\alpha \int_{\Omega} (n + p)^{3/2} dx. \quad (17)$$

3.2. Reaction Rate and Reaction-Drift-Diffusion System

According to [7, p. 17], the rate f is determined by

$$f = k_0 \exp\left(\frac{-2\beta\sqrt{I}}{1 + \delta\sqrt{I}}\right),$$

where β , δ , and k_0 are positive constants. We retain the definitions of u, n, p presented earlier. The isothermal model is presented as:

$$-\nabla \cdot [\epsilon \nabla u] + N_0 e^{u-v} - P_0 e^{w-u} = 0, \quad (18)$$

$$-\nabla \cdot [\mu_n e^{u-v} \nabla v] - f = 0, \quad (19)$$

$$-\nabla \cdot [\mu_p e^{w-u} \nabla w] + f = 0. \quad (20)$$

The system is augmented by boundary conditions of mixed type, as before. The open question pertains to solutions of the boundary value problem for the above system, satisfying electroneutrality and the generalized Gibbs condition. For concentrated ionic solutions, the Debye-Hückel theory must be extended [6, pp. 159–161]. This presents even greater challenges.

3.3. Extensions to the Nonisothermal Case

Most reactions in electrochemistry occur over a range of temperature variation. The system considered here would require expansion to include an energy conservation balance law. Extensions of the rudimentary theory outlined in this paper will eventually have to incorporate this very significant case.

3.4. Comparisons with Existing Thermodynamic Modeling

A considerable amount of study has been devoted recently to maximum entropy models. The field is too comprehensive to survey here. Essentially, moment closure is achieved by a maximum entropy principle for systems of equations defined by moments. Although no definitive statements can yet be made, it appears that maximum entropy is more restrictive than approaches based on partial convexity. This permits a family of admissible reactions and the trapping region defines a control parameter.

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