Information theory for analyzing heterogeneous electron transfer dynamics under steady-state conditions

Hyacinthe N. Randriamahazaka *

Interfaces, Traitements, Organisation et Dynamique des Systèmes (ITODYS), CNRS – UMR 7086, Université Paris-Diderot, Bâtiment Lavoisier, 15 rue Jean de Baïf, 75205 Paris Cedex 13, France

ARTICLE INFO

ABSTRACT

We develop a methodology based on information theory for studying the general characteristics of an electrochemical system from partial and incomplete information. We characterize a simple heterogeneous electron transfer under the conditions of a stationary regime in terms of a probability density function. This probability density function, which represents the observer's state of knowledge about the system rather than the state of the system itself, allows calculation of the information or statistical entropy. We show that irreversibility is not an intrinsic property of the system but a measure of some *distance* depending upon the relative entropy or Kullback–Leibler entropy and cross-entropy with respect to a reference, for instance, reversible conditions. The value of this *distance* is mainly determined by the ratio of two time constants characterizing the dynamics of the system. Data on ferrocene and ferric ions obtained in ultramicroelectrode experiments are given to illustrate the proposed methodology. Our objectives here are to present a different perspective on heterogeneous electron transfer reactions based on the information theory, and how the resulting formalism may be used to interpret experimental data.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Recent advances in nanotechnology, both bottom-up and top-down approaches, have made it possible to envisage complex systems [1–4]. Small systems of interest involve various kinds of materials (organic, inorganic, and biological components). A thorough understanding of the reactivity of and the interactions between molecules composing nanosystems is essential for nanotechnology. However, one of the main characteristics of nanosystems is their high surface-to-volume ratio. One has no easy access to the detailed topography of the surfaces which limit the active region of the sample. Until recently, scientists have lacked experimental methods to investigate the properties of small systems, such as the heat and work exchanged with their environment [5–7]. In other words, only limited overall quantities of the investigated system are known. Furthermore, the usually large fluctuations, relative to the mean energy value, experienced by these nanosystems affect their operation. Thus, the main problem is to determine when a model is adequate to explain a set of observations. The success of predictive tools depends on the accuracy of the theory used for such calculations.

Classical thermodynamics is restricted to equilibrium situations. It is correct for equilibrium systems, for reversible processes and for processes between equilibrium states. Absolute temperature and entropy are defined rigorously and unambiguously only in equilibrium. However, the range of application of classical thermodynamics is very narrow. Indeed, the existence of absolute temperature and of entropy outside equilibrium is simply assumed or a different hypothesis, for example local equilibrium, is used. This is the case of classical irreversible thermodynamics as developed by Onsager [8–10], Prigogine [11] and others [12]. It is well known that many systems are not in equilibrium although they reach a stationary state. One of the main problems of out-of-equilibrium thermodynamics is to define the state functions and to find relations between them, as well as evolution laws, in particular far from equilibrium [8,12]. Prigogine and Mazur [13] have extended thermodynamic concepts to irreversible phenomena in systems with internal degrees of freedom. However, the later theory is correct only near equilibrium. In order to extend the analysis of nonequilibrium systems, other formalisms have been proposed. One of them is information theory, a concept introduced by Shannon [14]. Information theory provides a powerful inference statistical methodology to describe the general properties of arbitrary systems on the basis of incomplete information.

The use of the information theory in the field of electrochemistry is scarce [15]. One of the main advantages of information theory is its capability of describing the equilibrium and non-equilibrium states in the framework of a unified scheme. In this work, we analyze a non-equilibrium process in terms of internal

* Corresponding author. Tel.: +33 (0)1 57 27 72 01.
  E-mail address: randria@itodys.jussieu.fr
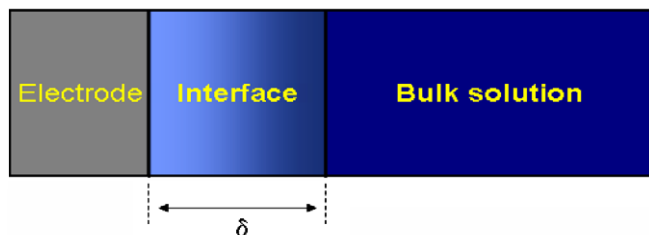
Scheme 1. Schematic representation of the system showing the interface region (δ is the thickness of the diffusion layer) where a concentration gradient occurs.

coordinate variables. We consider an electrochemical reaction–diffusion system maintained at a fixed temperature. We study a simple heterogeneous electron transfer under the conditions of a stationary regime characterized by a probability density function $P(\xi, \varepsilon)$ [16], where ξ and ε are the degree of advancement and the dimensionless potential, respectively. It should be noted that the system under investigation (Scheme 1) is a driven system one which evolves via a series of non-equilibrium stationary states. The latter process is due to the variation of the controlling parameters, for instance, the applied potential *E*.

The modern approach to the evaluation of measurement data is based on the mathematical formulation of the idea that any kind of information relevant for inferencing the measurand generates a corresponding state of knowledge about the measurand. Nowadays, there is a great interest to study the charge transfer in micro- and nanosystems. However, it is well known that experimental data obtained for these systems are often tainted with noise. The aim this work is to formulate a methodology that allows us to understand the general characteristics of a system from partial and incomplete information. Indeed, a general analytical formalism for dealing with small systems, regardless of their nature, is still lacking. Since the information is incomplete, a probabilistic approach will be used. There is only one way to assign any probability: logical analysis, i.e. self-consistent analysis of the available information. Logical analysis may be applied in the form of the principle of maximum entropy to yield probabilities [17–19]. The maximum entropy gives a class of probability density function for which sufficient statistics exist. The sufficient statistics are the sample moments corresponding to the constraints that were used in the maximum entropy calculation. Here, we present an overall approach based on a probabilistic approach. We attempt to analyze a driven electrochemical system occurring under steady-state conditions in terms of information entropy for a microsystem. In this report, we describe the use of the information theory formalisms to analyze the redox kinetics of ferrocene–ferricinium or ferric–ferrous systems on a platinum ultramicroelectrode. The redox properties of these systems are fairly well understood. The goal of the present study is thus not so much to reveal new features of this particular redox system but rather to examine the utility of the probability density function and information (statistical) entropy for characterizing redox kinetics. We hope that the perspective presented herein will be useful for advancing the qualitative and quantitative analysis of charge-transfer reactions when only partial information is available.

2. Background

Bayesian probability is one of the major practical frameworks for reasoning under uncertainty. It is a systematic way of approaching a problem in which one is confronted with incomplete knowledge about the system. The typical use of Bayesian probability is an *input–output* information-processing activity.

The *input* concerns the data, measurements, relationships, and constraints that provide information about the system. The *output* is the analysis of the system in order to understand and interpret what is going on in the system. Thus, Bayesian probability theory provides an interesting way to process information from input to output under uncertainty. The information about the variables in the system is a single-valued function, commonly known as the probability density function, over the *N*-dimensional base space of variables. If the system is, at a particular instant, in a particular state the information functions on the variables of the system have particular values. Thus, the set of all possible values that the state variables can have is called the state space.

The combination of a set of variables, their information, and relationships functions make it possible to construct a model. The collection of information comes from various sources: prior knowledge about the system (such as the physical laws that it obeys, or known initial conditions), measurements and data from the system. However, it should be noted that the probability density function representing the information about a given system does not represent the *real state* of that system; it represents information that the *observer* of the system has collected about the system. There are three different types of information that must be incorporated into the probability assignment: parameter ranges, knowledge of the mean *m* and standard deviation σ of the probability density function. Lacking any detailed information, one has to resort to the inference method. Maximum entropy methods have been developed in this context [14]. The principle of maximum entropy, as a method of statistical inference, is due to Jaynes [19]. This principle leads to the selection of a probability density function which is consistent with our knowledge and introduces no unwarranted information. According to this principle, if we are seeking a probability density function to certain constraints (e.g. a given mean or variance), we shall choose the density function satisfying those constraints which has the highest possible entropy. Thus, the probability density function can be viewed as a numerical measure of the plausibility that some individual situation develops in certain ways. The principle of maximum entropy is a rule for assigning probabilities in a rational and unbiased way. To this end, we use the Lagrange multiplier to maximize the entropy.

In the present case, we analyze a simple heterogeneous electron transfer:

$$\text{Red} \rightleftharpoons \text{Ox}^+ + 1e^- \tag{1}$$

where Red and Ox^+ are the reduced and the oxidized forms of the electro-active species, respectively. Generally, the simplest electrode process consists of at least the following elementary steps: (i) transport of the electro-active species between the bulk electrolyte solution and the adjacent region of the electrode, and (ii) electrochemical reactions. In our case, the solution contains an excess of supporting electrolyte in order to increase its electrical conductivity and to minimize the ohmic potential drop between the electrode and solution. Thus, mass transport is governed by diffusion. Under steady-state conditions, the fluxes of all species are constant and are equal to the specific value at the working electrode surface. In our previous work [16], we have introduced a dimensionless variable ξ_{ox} that allows us to calculate the degree of advancement of the electro-oxidation described in Eq. (1) as:

$$\xi_{\text{ox}} = 1 - \frac{[\text{Red}]_{\text{el}}}{[\text{Red}]_{\text{b}}} \tag{2a}$$

where $[\text{Red}]_{\text{el}}$ is the concentration of Red at the electrode surface, and $[\text{Red}]_{\text{b}}$ is the concentration of Red in the bulk solution. The degree of advancement ξ_{ox} (for the electro-oxidation) can be also expressed as