ELECTROCHEMISTRY: THEORETICAL FOUNDATIONS

QUANTUM AND STATISTICAL MECHANICS, THERMODYNAMICS, THE SOLID STATE

Jerry Goodisman

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PREFACE

Matter is composed of charged particles. The chemical properties of matter are determined by this fact, because the Coulombic interaction is the only interparticle potential in the Schrödinger equation. The Coulombic interaction thus determines electronic structure and hence chemistry. However, this fact need not be dealt with explicitly—except in electrochemistry. Electrochemical phenomena reflect directly the electrostatic interaction between the particles that comprise matter. Yet, most of electrochemical theory was built on a macroscopic level, without explicit consideration of the fundamental charged particles and their properties. Progress in quantum chemistry, statistical mechanics, and so on, has made it possible to provide a description on the molecular level of some of the macroscopic electrochemical properties and laws. In this book, we describe some of what has been developed in this domain and try to relate the molecular description to the macroscopic description and to the observed phenomena of electrochemistry.

In the traditional (thermodynamic) description of electrochemistry, the cell potential is introduced as a consequence of the existence of a cell reaction that is not at equilibrium. The cell potential is subsequently divided into contributions of the two half-cells making up the cell and eventually into individual electrode potentials, related to the two half-cell reactions. The more modern approach, as exemplified in the books by Bockris, begins from a physical description on the molecular level of the electrochemical interfaces and of conducting media. The electrochemical cell potential is then a sum of actual potential differences across the interfaces and (when current is flowing) across homogeneous regions, which, when linked together in series, make up the cell.

Since understanding what goes into a cell potential involves knowledge of solid-state and liquid-state physics and chemistry, statistical mechanics, thermodynamics, quantum mechanics, and other areas of science, study of electrochemistry ought to be central to physical chemistry. This is not at all what one would conclude from the way the subject is discussed in many physical chemistry texts. Many authors, far from relating the subject to the other areas, discuss electrochemistry as a "special topic" with its own strange and not very well founded lore. As a result, "distaste and disgust are the predominant emotions that the normal student feels for electrochemistry" (Albery 1975). In this book we try to discuss basic material in electrostatics, thermodynamics, and statistical mechanics, as well as the electrochemistry itself, in the hope of helping to alleviate this problem.

We hope that our presentation may be useful to chemists and physicists desiring to learn about the subject, and to those who are involved in teaching it to others, as well as to electrochemists whose knowledge of quantum mechanics and molecular science lags behind their knowledge of electrochemistry. The book is, in fact, the attempt of the author (a quantum chemist by training) to get it all straight for himself. He hopes, therefore, that others may find it useful and that it may help interest scientists in the problems at the electrochemical interface.

It is convenient to separate electrochemistry into phenomena of conduction, which occur in homogeneous systems, and phenomena occurring at the electrochemical interface, which is the macroscopically negligible region between two different homogeneous media. We are concerned mainly with the latter part. In the interface, charge density, particle density, electrical potential, and other intensive properties vary in space, sometimes extremely rapidly. The extreme inhomogeneity constitutes the main difficulty in generating theories and descriptions of the interface.

Chapter 1 gives a general description and overview of electrochemistry, with only minimal theoretical framework. Chapter 2 discusses thermodynamics and electrostatics, the concepts of which are used for macroscopic descriptions of the interface. Chapter 3 turns to statistical mechanics, whose province it is to relate molecular-level concepts to macroscopic quantities. Succeeding chapters (4, 5, and 6) deal with the structure of surfaces and interfaces, in the framework of the first few chapters. The remainder of the book discusses dynamical processes: diffusion (Chapter 7) and electrochemical kinetics. In Chapter 8, the processes of electrode kinetics are discussed. Chapter 9 considers the quantum mechanical aspects of electron transfer, which are incorporated in the theories of electrode reactions discussed in Chapter 10.

JERRY GOODISMAN

Syracuse, New York
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1

ELECTROCHEMISTRY

A. INTRODUCTION: THE ELECTROCHEMICAL CELL

An electrochemical cell is a collection of chemical reactants connected to the surroundings by two terminals (electronic conductors) of identical composition. The arrangement of the reactants inside the cell is such that, for a chemical reaction between some of them to occur, electrical current must flow in the surroundings from one terminal to another. If, when the circuit is closed by making electrical contact between the terminals, the chemical reaction occurs spontaneously with a current flow resulting, we refer to the cell as a *galvanic cell*. If an external source of electrical potential is introduced between the terminals, with the current produced being accompanied by the chemical reaction, we refer to the cell as an *electrolytic cell*. We may suppose in either case that a voltmeter and an ammeter are connected to the cell so that one can measure the difference in electrical potential between the terminals (this is why we require them to be of identical composition) and the current, if any, flowing between them.

Inside the cell, there must be a physical separation between reactants to prevent direct reaction from occurring. This requires that several phases be present, with mixing being hindered by some barrier or by the nature of the phases. It is conventional to specify the composition of the cell by listing the phases from the left-hand terminal to the right-hand terminal, with a vertical line indicating a phase boundary. Thus the Daniell cell, the cell reaction of which is the oxidation of Zn to Zn^{2+} by Cu^{2+} ion, is represented as

$$\mathrm{Cu}\,|\,\mathrm{Zn}\,|\,\mathrm{ZnSO_4}(a_1)\,\|\,\mathrm{CuSO_4}(a_2)\,|\,\mathrm{Cu} \qquad [1]$$

if the terminals are copper (a_i is an activity). The double vertical line indicates a liquid–liquid junction across which the electrical potential difference has been eliminated, or is assumed to be negligible. So long as Cu^{2+} ions do not reach the Zn electrode, direct chemical reaction does not occur. The liquid–liquid junction prevents such mixing while allowing electrical contact between the solutions. This is sometimes accomplished by inserting a concentrated solution or gel containing an inert electrolyte between the two solutions of the cell.

The electromotive force (emf) of a cell, in the most commonly used convention, is the electrical potential of the terminal on the right minus the electrical potential of the terminal on the left, when no current is flowing (open circuit). The value and sign of the electromotive force $\mathcal{E}$ indicate the spontaneity of the chemical reaction that will occur on closing the circuit. If $\mathcal{E}$ is positive, as is the case for the Daniell cell as given in equation [1], the tendency will be for positive electrical current to flow in the surroundings (external circuit) from the right-hand terminal to the left-hand terminal, that is, electrons will enter the cell from the surroundings through the right-hand terminal and leave the cell through the left-hand terminal. Thus, within the cell, reduction will occur at the right-hand electrode (e.g., $Cu^{2+} + 2e^- \rightarrow Cu$) and oxidation will occur at the left-hand electrode (e.g., $Zn \rightarrow Zn^{2+} + 2e^-$). The value of the emf depends, of course, on the composition and arrangement of the phases constituting the cell.

Since there are no electrical fields within any phase when no current is flowing, each phase is an equipotential at open circuit, so that the emf involves a sum of potential differences across phase boundaries. For the Daniell cell, one may write

$$\begin{aligned} \mathcal{E} &= \phi^{(R)} - \phi^{(L)} \\ &= [\phi^{(R)} - \phi^{(2)}] + [\phi^{(2)} - \phi^{(1)}] \\ &\quad + [\phi^{(1)} - \phi^{(\mathrm{Zn})}] + [\phi^{(\mathrm{Zn})} - \phi^{(L)}] \qquad [2] \end{aligned}$$

where R and L identify the right-hand and left-hand copper terminals, respectively, and 1 and 2 identify the $ZnSO_4$ and $CuSO_4$ solution phases, respectively. The assumption of no liquid junction potential means $\phi^{(2)} - \phi^{(1)} = 0$. The potential difference between zinc and copper in contact, for example, $\phi^{(\mathrm{Zn})} - \phi^{(L)}$, is a property of this combination of metals, whereas each of the two metal–solution potential differences should depend on the solution concentration as well as the chemical natures of metal and solution. The fact that it is experimentally impossible to measure the difference of electrical potential between two chemically nonidentical phases will not prevent us from discussing it.

Indeed, one of our major concerns is to describe the progress that has been made in understanding the interphase potential differences and in explaining them in terms of the properties of the two phases in contact. On a molecular level, of course, there is no sharp boundary between phases, but rather a region across which intensive properties vary in values from one phase to another. The structure of this region depends upon the same kinds of intermolecular interactions that determine the structure of the adjacent homogeneous phases. We will also be concerned with understanding how the potential difference between phases may be altered by changing the electrical conditions, that is, by introducing electrical charge, or, where possible, by changing the composition of the phases. The electrical charge, too, is located at interphase boundaries and may be described as a surface charge density, because there cannot be a nonzero volume charge density through a homogeneous phase. If there are no electric fields in the homogeneous phases, the total surface charge density at each interface must be zero, so that there must be compensating layers of positive and negative charge density (''double layer''), thus giving rise to a difference of electrical potential but not to any electrical field outside the interface. Understanding double layers will be another important concern.

When current is flowing through an electrochemical cell, there are electrical fields within the homogeneous phases, which contribute to the overall potential drop across the cell. At the same time, of course, the electrical structure of the interphase regions may be altered. Within the homogeneous phases, we are concerned with the phenomena of conductivity. At each junction between two phases, there is a charge transfer, involving a heterogeneous chemical reaction, to be analyzed. Writing the overall cell reaction for the Daniell cell,

$$\mathrm{Cu^{2+}(aq) + Zn}(s) \rightarrow \mathrm{Cu}(s) + \mathrm{Zn^{2+}(aq)}$$

does not present any picture of the complicated processes involved, whose overall effect is the transfer of electrical charge through the cell and the conversion of reactants to products. It is these processes that must be understood if one is to understand the way in which the current flowing through a galvanic or electrolytic cell depends on the difference in electrical potential between the terminals. Of course, the current is simply related to the rate of the overall cell reaction by Faraday's laws, which state that the rate at which a product is formed or a reactant consumed is given by the current through the cell divided by the number of elemental electrical charges per molecule of substance. Here, 1 elemental charge = charge of an electron = 1 faraday ÷ Avogadro's number, where 1 faraday ($\mathfrak{F}$) = 96,493 coulombs/mole (C/mol) and $N_{\mathrm{Avogadro}} = 6.0225 \times 10^{23}\ \mathrm{mole}^{-1}$. These laws, like the cell reaction itself, give no information about what is really happening.

In the remainder of this chapter, we review the phenomena of electrochemistry, which the rest of the book attempts to explain or at least discuss. We first consider the emf, discussing the Nernst equation and introducing electrochemical potentials and their chemical and electrical parts. Not much more than elementary ideas will be presented regarding the structure of the interfacial regions. Then we will consider, still from a macroscopic point of view, something of what happens when the external circuit of a cell is closed. Subsequent chapters will deal with the above-mentioned phenomena, after the introduction of a molecular description of the electrochemical interface, and consider the connection between the molecular description and the macroscopic laws.

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B. ELECTROMOTIVE FORCE AND HALF-CELLS

If we limit ourselves to open circuit, so that no current is passing through our electrochemical cell, we can measure only the difference of electrical potential between the terminals, that is, the emf, defined by

$$\mathcal{E} = \phi^{(R)} - \phi^{(L)}$$

where R and L indicate the right-hand and left-hand terminals, respectively. If $\mathcal{E}$ is nonzero, short-circuit of the cell will lead to a current flow and a chemical reaction within the cell: Oxidation will take place at one electrode and reduction will take place at the other. This would be an irreversible process: The occurrence of reaction indicates the absence of equilibrium. However, we may consider that, before closing the circuit, one has equilibrium everywhere within the cell and that this equilibrium may be maintained at closed circuit if an external voltage source equal and opposite to $\mathcal{E}$ is inserted between the terminals, stopping the current that would otherwise flow. If the external voltage differs infinitesimally from $\mathcal{E}$, an infinitesimal current will flow. Under these circumstances, the transfer of charge around the circuit, with the accompanying chemical reactions within the cell, will be occurring reversibly.

The work that the cell performs on the surroundings may then be equated to the decrease in the cell's free energy. Assuming the process occurs at constant pressure, we have

$$(-\Delta G_M)\, dx = \mathcal{E}\, dq \qquad [3]$$

where ΔG_M is the free energy change when the amount of reaction, x, changes by 1 mole at the given values of intensive parameters; dx represents an infinitesimal amount of reaction; and dq is the amount of charge transferred from the terminal on the right to the terminal on the left, through the external circuit, when dx degree of reaction occurs. The changes in the numbers of moles of reactants and products are related to dx by the stoichiometric coefficients, and the relation of dq to dx is obtained by writing the reaction as a sum of oxidation and reduction half-reactions. For the Daniell cell we have

Oxidation: $\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2e^-$ (left)

Reduction: $\mathrm{Cu}^{2+} + 2e^- \rightarrow \mathrm{Cu}$ (right)

so 1 mole of reaction involves 2 faradays ($\mathfrak{F}$) of electricity in the form of electrons. Then $dq = 2\mathfrak{F}\, dx$ and

$$\Delta G_M = -n\mathfrak{F}\mathcal{E} \qquad [4]$$

where $n = 2$ for the Daniell cell as written. Inserting this into the Gibbs–Helmholtz equation, $\Delta G = \Delta H + T(\partial \Delta G/\partial T)$ we find

$$\Delta H = -n\mathfrak{F}\mathcal{E} + n\mathfrak{F}\frac{\partial \mathcal{E}}{\partial T} \qquad [5]$$

so that from the cell emf, as a function of temperature, one can calculate the heat of reaction.

The free energy change for a reaction is given by

$$\Delta G_M = \sum_i \mu_i \nu_i$$

where the chemical potential μ_i of each reactant or product is multiplied by the stoichiometric coefficient ν_i, taken from the cell reaction, with ν_i positive for products and negative for reactants. Thus, for the Daniell cell,

$$\begin{aligned} 2\mathfrak{F}\mathcal{E} &= \mu(\mathrm{Zn}) - \mu(\mathrm{Zn}^{2+}) - \mu(\mathrm{Cu}) + \mu(\mathrm{Cu}^{2+}) \\ &= -\mu(\mathrm{ZnSO_4}) + \mu(\mathrm{CuSO_4}) + \mu(\mathrm{Zn}) - \mu(\mathrm{Cu}) \end{aligned}$$

where the reaction is considered as if it occurred directly.

If the chemical potential for each substance is written as its value for the standard state of that substance plus a term involving its activity a_i, we have

$$\Delta G_M = \sum \nu_i \mu_i^0 + RT \sum \nu_i \ln a_i$$

Since $\Delta G_M = -n\mathfrak{F}\mathcal{E}$, it is natural to represent the first summation on the right as $-n\mathfrak{F}\mathcal{E}^0$, where $\mathcal{E}^0$ is the emf the cell would exhibit if all reactants and products were in their standard states. Then

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{n\mathfrak{F}} \sum \nu_i \ln a_i \quad . \qquad [6]$$

which is a form of the Nernst equation. If the reaction were at equilibrium, the value of the summation would be the logarithm of the equilibrium constant K:

$$\sum \nu_i \ln a_i = \ln \left(\prod a_i^{\nu_i} \right) = K \qquad [7]$$

In the electrochemical cell, the existence of this condition is revealed by an emf of zero: There is no tendency for electron flow or chemical reaction on connecting the terminals. Thus

$$\mathcal{E}^0 = \frac{RT}{n\mathfrak{F}} \ln K \qquad [8]$$

which relates the standard cell potential to the equilibrium constant.

It is also possible to write $\mathcal{E}$ as a sum of two contributions, one for each half-reaction. This is useful as a "bookkeeping device," with *no* implication that the actual potential difference across the cell is the sum of terms representing potential differences across the half-cells (we discuss such a separation later). From here on, we follow the convention of writing all half-cell reactions as reductions (electrons appear on the left-hand side of the reaction equation), so that the cell reaction is obtained by subtracting the reaction for the left-hand half-cell from the reaction for the right-hand half-cell, just as $\mathcal{E}$ is obtained by subtracting the potential of the left-hand terminal from the potential of the right-hand terminal. Thus, if the reaction takes place in the direction it is written, reduction will occur at the right-hand electrode and oxidation will occur at the left-hand electrode. For the general cell reaction

$$\mathrm{O}_R + \mathrm{R}_L \rightarrow \mathrm{R}_R + \mathrm{O}_L$$

(where O and R refer to oxidized species and reduced species, respectively, and subscripts R and L refer to right-hand and left-hand half-cells, respectively), the half-cell reactions are written as

$$\mathrm{O}_R + ne^- \rightarrow \mathrm{R}_R \quad \text{on the right}$$

and

$$\mathrm{O}_L + ne^- \rightarrow \mathrm{R}_L \quad \text{on the left}$$

their difference being the cell reaction. Separating chemical potentials for the two half-cell reactions, we have

$$\begin{aligned} -n\mathcal{F}\mathcal{E} &= \sum^{R} \nu_i \mu_i + \sum^{L} \nu_i \mu_i \\ &= -n\mathcal{F}(\mathcal{E}^{R}_{1/2} - \mathcal{E}^{L}_{1/2}) \end{aligned} \qquad [9]$$

where the electrons do not appear. The emf of the cell has thus been written as the difference of terms referring to the half-cells.

Now consider several half-cells that may be combined into cells:

$$\mathrm{O}_{\mathrm{I}} + ne^- \rightarrow \mathrm{R}_{\mathrm{I}}$$

$$\mathrm{O}_{\mathrm{II}} + ne^- \rightarrow \mathrm{R}_{\mathrm{II}}$$

$$\mathrm{O}_{\mathrm{III}} + ne^- \rightarrow \mathrm{R}_{\mathrm{III}}$$

We may suppose that each half-cell reaction has been multiplied by some integer to make the number of electrons the same for each, so that any one may be subtracted from another to give a cell reaction. If I is used as the left-hand half-cell and II is used as the right-hand half-cell, the cell reaction will be the sum of reaction II and reaction I in reverse, with molar free energy change

$$\Delta G_{\text{I-II}} = \sum^{\text{II}} \nu_i \mu_i - \sum^{\text{I}} \nu_i \mu_i = -n\mathfrak{F}\mathcal{E}_{\text{I-II}}$$

If III is used on the right instead of II, we will have

$$\Delta G_{\text{I-III}} = \sum^{\text{III}} \nu_i \mu_i - \sum^{\text{I}} \nu_i \mu_i = -n\mathfrak{F}\mathcal{E}_{\text{I-III}}$$

and if II is used on the left and III is used on the right,

$$\Delta G_{\text{II-III}} = \sum^{\text{III}} \nu_i \mu_i - \sum^{\text{II}} \nu_i \mu_i = -n\mathfrak{F}\mathcal{E}_{\text{II-III}}$$

Obviously, the free energy changes obey

$$\Delta G_{\text{II-III}} = \Delta G_{\text{I-III}} - \Delta G_{\text{I-II}}$$

so that the emf's of the cells obey

$$\mathcal{E}_{\text{II-III}} = \mathcal{E}_{\text{I-III}} - \mathcal{E}_{\text{I-II}} \qquad [10]$$

This allows the possibility of assigning "half-cell potentials" to the half-cell reactions, such that the emf of any cell will be equal to the difference of the potentials for the half-cells of which it is composed: $\mathcal{E}^{R}_{1/2} - \mathcal{E}^{L}_{1/2}$.

Writing chemical potentials in terms of activities according to

$$\mu_i = \mu_i^0 + RT \ln a_i$$

and defining $\mathcal{E}^{0}_{1/2}$ as the value of the half-cell potential when all participants in the half-cell reaction (electrons not included) are at unit activity means that

$$\mathcal{E}_{1/2} = \mathcal{E}^{0}_{1/2} - \frac{RT}{n\mathfrak{F}} \sum \nu_i \ln a_i \qquad [11]$$

Here the stoichiometric coefficients correspond to the participants in a half-cell reaction, written as a reduction. When we combine two relations like equation [11] to obtain the emf of a full electrochemical cell, we recover

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{n\mathfrak{F}} \sum \nu_i \ln a_i \qquad [12]$$

where the sum now includes all participants in the cell reaction, that is, both half-cells, with those of the left-hand half-cell having ν_i of sign opposite to what appears in the half-cell reaction. It may also be noted that multiplying a half-cell reaction by a constant c does not change $\mathcal{E}^0_{1/2}$, because n and all ν_i are multiplied by c. The standard half-cell potentials $\mathcal{E}^0_{1/2}$ are given in tables as standard half-cell reduction potentials (or as standard oxidation potentials if half-cell reactions are written as oxidations instead of reductions). Since only differences in the values of $\mathcal{E}_{1/2}$ are meaningful, the value of one may be arbitrarily assigned; that corresponding to the standard hydrogen electrode (SHE), with half-cell reaction

$$\tfrac{1}{2}\mathrm{H_2}(g,\ 1\ \mathrm{atm}) + e^- \rightarrow \mathrm{H}^+(a = 1)$$

is by convention given the value zero. Clearly, the values given to the other half-cell reduction potentials depend on this convention and have no absolute meaning.

C. ELECTROCHEMICAL POTENTIALS AND ELECTRICAL POTENTIALS

The chemical potentials in the preceding equations include those for charged species. If the chemical potential of a substance is defined as the work necessary to introduce 1 mole of the substance into a large system, we note the following: (a) There is a problem of measurability for chemical potentials of charged species; (b) the chemical potential is most likely dependent on the electrical potential of the system. With respect to (b), we note that a cell reaction is written as if all the substances were in the same medium, with the reaction occurring outside of the electrochemical cell. Since the total charge of the reactants must equal the total charge of the products, changing the electrical potential of the medium would affect reactants and products equally, leaving ΔG_M unaffected. Furthermore, one can always add oppositely charged species to both sides of the equation for the cell reaction to produce one involving neutral species. For example, the Daniell cell reaction,

$$\mathrm{Zn} + \mathrm{Cu}^{2+}(\mathrm{aq}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq}) + \mathrm{Cu}$$

is quite equivalent to

$$\mathrm{Zn} + \mathrm{Cu}^{2+}(\mathrm{aq}) + \mathrm{SO}_4^{2-}(\mathrm{aq}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq}) + \mathrm{SO}_4^{2-}(\mathrm{aq}) + \mathrm{Cu}$$

or just

$$\mathrm{Zn} + \mathrm{CuSO_4}(\mathrm{aq}) \rightarrow \mathrm{ZnSO_4}(\mathrm{aq}) + \mathrm{Cu}$$

with the electrical state of the medium being irrelevant.

With respect to (a), we may say that, although individual chemical potentials for charged species cannot be measured, they may still be considered theoretically.

However, the work needed to introduce a charged species into a phase must depend on the electrical state of the phase, which leads to the concept of electrochemical potential. The electrochemical potential $\tilde{\mu}_i$ is defined as the work necessary to transfer 1 mole of species i into a phase from an infinitely dilute gaseous state at an infinite distance from the phase, or the free-energy change accompanying such a transfer. Thus, if two phases are in contact so species i can move from one to another, the equilibrium condition is that $\tilde{\mu}_i$ be the same for both.

The value of the electrochemical potential obviously depends on the phase: In addition to the work against the short-range (chemical) forces within the phase, there will be electrical work against the long-range Coulombic forces, if species i is charged. We write

$$\tilde{\mu}_i^{(P)} = \mu_i^{(P)} + q_i\mathfrak{F}\phi^{(P)} \qquad [13]$$

where P refers to the phase, $\mu_i^{(P)}$ is the chemical potential of substance i in phase P, and $\phi^{(P)}$ is the electrostatic potential inside phase P. This is the potential referred to in the definition of the emf. Its value is relative to zero for a vacuum an infinite distance away.

Since the same constituents of matter are responsible for its electrical charge and its chemical properties, the separation implied by equation [13] cannot be completely rigorous, but simple calculations show that the amount of electrons required to give even a small, but macroscopic, amount of matter a potential of the order of volts is far too small to affect the chemical properties. The potential $\phi^{(P)}$ is called the *inner electrical potential* or *Galvani potential* of phase P and is an average over a region large compared to molecular size. The chemical potential $\mu_i^{(P)}$ represents the work required to transfer a mole of i to P in the case $\phi^{(P)} = 0$.

It may not be possible in a particular case to realize the situation $\phi^{(P)} = 0$. This is because an electrical potential difference is likely to exist between a point just outside the surface of a phase and a point just inside the surface. This surface potential results from the structure of the inhomogeneous surface region, in which large electric fields may exist; this structure, which is governed by the interactions between constituents of the phase, is inseparable from the bulk properties of the phase. It is usual to express this by

$$\phi^{(P)} = \chi^{(P)} + \psi^{(P)} \qquad [14]$$

where $\chi^{(P)}$ is the surface potential and $\psi^{(P)}$ is the outer potential or Volta potential. The electrical work required to transfer a charged species j from infinity to the interior of P is thus the sum of the work $q_j\psi^{(P)}$ required to bring it to a point just outside P (macroscopic distance of zero) and the work associated with the surface potential $\chi^{(P)}$. The value of $\psi^{(P)}$ is associated with the charge of P.

The difference in outer or Volta potentials between two chemically different phases is measurable (since it involves the work required to move a test charge through vacuum from one phase to the other), and hence the value of the Volta

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