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Supramolecular Electrochemistry

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To our parents

Angel, Barbara, Edward, Ellen and Emilia

in thanks for their support of our curiosity
and pursuit of knowledge

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Preface

Supramolecular chemistry has different meanings for different people, and, perhaps, because of this ambiguity it is best to follow Professor Lehn's definition. In his words, supramolecular chemistry concerns the "chemistry beyond the covalent bond". This definition rightfully places emphasis on the importance of intermolecular forces present in supramolecular systems. From simple host-guest complexes to infinitely more complicated supramolecular assemblies described in the recent literature, intermolecular forces are at the core of all relevant supramolecular systems. Research in supramolecular chemistry already has a long and productive history and many reviews and several books have been devoted to this field of chemistry. In spite of the influence and importance that electrochemical techniques and concepts have had in the development of the field, when we started this work there were no monographs available on supramolecular electrochemistry. This book represents a modest attempt to correct this state of affairs.

In launching a project such as this one, it is important to set clear goals. Our primary and foremost purpose was to provide the research community in supramolecular chemistry with an accessible and readable summary on the use of electrochemical techniques and the applications of electrochemical concepts to this new research area. A second purpose was to increase the level of interest in supramolecular systems from the electrochemical community. The book is thus intended as a tool to build bridges between these two rather separate communities and to foster some degree of cross-fertilization between the two research areas. In order to meet these goals, and due to the wide diversity of topics that we wanted to address, we could not, therefore, provide a comprehensive or thorough description of the subject matter. As is usually the case, we were forced to make many compromises concerning the selection of topics and the depth of coverage. The first seven chapters of the book are intended as an introduction to electrochemical techniques. Readers with a reasonable background in electrochemistry can probably skip these chapters. The remaining chapters address the electrochemistry of the most important types of supramolecular systems. Overall, the book should be useful to graduate students and postdocs, as well as more experienced researchers who are interested in expanding their research horizons at the frontier of electrochemistry and supramolecular chemistry.

As stated above, this book does not even attempt a comprehensive coverage of the research topics presented. Therefore, literature citations were selected by the authors using very personal and, perhaps, seemingly arbitrary

criteria. We wish to apologize in advance to all those who feel that their work has not been appropriately represented here: this book is merely our personal view of the research landscape.

Miami, June 1999 *Angel Kaifer and Marielle Gómez-Kaifer*

Acknowledgments

The authors owe their involvement in this research field to many people. First, they wish to express their gratitude to their common doctoral advisor, Professor Luis Echegoyen, who inspired them with his great enthusiasm and love for science. Both authors have been associated with the group of Professor Allen J. Bard, to whom they are indebted for his lucid teachings on electrochemistry, and his insights into the general importance of electrochemistry and the diverse ways in which it can be applied to almost any field of chemical research. We are fortunate to have been influenced by Professor Bard's approach to research, which embodies all the best of collegiality and the true spirit of scientific endeavor.

Over the years the authors have worked, discussed, and in many cases published, with a number of researchers in this field. Their contributions are important to this book and are reflected at many points throughout the manuscript. At the risk of missing someone, we wish to thank Jerry Atwood, Carmen María Casado, Alessandro Casnati, Cecil Criss, Isabel Cuadrado, Jeff Evanseck, George W. Gokel, David Gutsche, Moisés Morán, David Reinhoudt, Neil Spencer, J. Fraser Stoddart, Rocco Ungaro, and Frank van Veggel. The Kaifer group's contribution to research in the field stems from the hard work of graduate students and postdoctoral associates. Their work cannot be overestimated. Julio Álvarez, Anna Bernardo, Richard Bissell, Claudia Cardona, René Castro, Emilio Córdova, Luis Godínez, Tim Goodnow, Mei Han, Rahimah Isnin, Jing Li, Jian Liu, Sandra Mendoza, Armen Mirzoian, Carlos Peinador, María Rojas, Esteban Román, Yun Wang and Litao Zhang deserve our special thanks.

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Contents

1 Fundamentals of Electrochemical Theory

Electrochemistry is a branch of science with a long and prestigious history. The theoretical foundations of electrochemistry were laid out by Faraday, Volta, Galvani and many other prominent scientists; their names are now routinely used to designate constants, units, processes, or types of cells. Electrochemistry can be defined in a very general way as the study of chemical reactions to produce electric power or, alternatively, the use of electricity to affect chemical processes or systems. The first perspective concerns the so-called *galvanic* cells, while the second relates to *electrolytic* processes. Both have tremendous practical importance, industrially as well as in everyday life. From the electrolytic preparation of chlorine to the widespread use of batteries, electrochemistry is a branch of science that has a clear and marked impact in everyone's life. While the user of a cellular phone whose battery dies in the middle of an important conversation might all too clearly perceive the limitations of electrochemical technology, it is equally true that developments and advances in electrochemical science hold the key to some important technological breakthroughs. Electric cars afford the primary example for this situation because attractive operational characteristics --that will make them competitive with vehicles based on the internal combustion engine-- require batteries with higher power densities and peak power outputs. As these better batteries become available, the feasibility and popularity of electric vehicles should improve.

1.1 Cell Potentials and Electrochemical Reactions

As the simplest type of chemical reaction, electron transfer processes are at the core of electrochemistry. Electrons, the key players in these phenomena, are also the carriers of electricity in metallic and semiconductor circuits. Therefore, the connection between chemistry and electricity is obvious. The science of electrochemistry has its origins in the fact that oxidation-reduction reactions can be performed in ways that allow the direct harvesting of the free energy released in these processes. Consider, for instance, the following spontaneous reaction

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \qquad (1)$$

While it is possible to immerse Zn metal in a solution of Cu(II) ions and observe the oxidation (dissolution) of the Zn metal along with the simultaneous reduction of the Cu(II) ions (to form metallic Cu deposits), the same overall reaction can be carried out by immersing a Zn strip in a solution of Zn(II) ions

and a Cu strip in a solution of Cu(II) ions (see Fig. 1.1). To start the reaction, one only needs to establish pathways for the charges (electrons and ions) to circulate between the sites at which the Zn oxidation and Cu(II) reduction processes take place. This is accomplished by setting up a salt bridge to establish electrical contact between the two solutions. The salt bridge allows the circulation of ions between the two solutions while preventing their mixing. Under these conditions a potential difference between the Zn and Cu strips develops. If the circuit is closed externally, that is, if a so-called electrical "load" is connected to the metal electrodes, the existing potential difference will give rise to a current, a flow of electrons moving from the Zn electrode (negative pole) to the Cu electrode (positive pole). The free energy ΔG^o of the overall chemical reaction taking place in the cell can be readily calculated as

$$\Delta G^o = -nFE^o_{cell} \tag{2}$$

where n is the total number of electrons transferred in the reaction, F is Faraday's constant and E^o_{cell} is the standard cell potential of the cell.

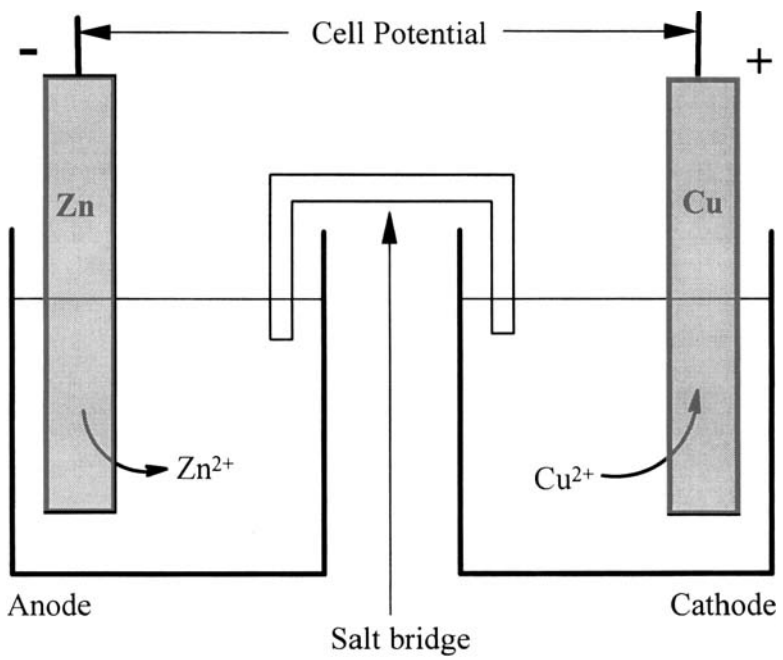

Figure 1.1: Components of a Galvanic Cell.

Electrochemical reactions are heterogeneous in nature as they take place at interfaces, usually metal-solution boundaries. These active interfaces are usually referred to as *electrodes*. By definition, an electrode where a reduction

(uptake of electrons by a solution species) takes place is called a *cathode.* Conversely, an *anode* is an electrode where an oxidation (loss of electrons by a solution species) occurs. Applying these definitions to the electrodes of the galvanic cell in Fig. 1.1, it is straightforward to conclude that the Zn electrode is the anode and the Cu electrode serves as the cathode.

A net electrochemical reaction implies transfer of charge across the corresponding metal solution boundary and the flow of current across the electrode. The current i, a basic electrical quantity, affords an instantaneous measurement of the rate of the electrochemical reaction according to equation (3)

$$i = nFAr \tag{3}$$

where n is the number of electrons transferred in the interfacial reduction or oxidation process, F is Faraday's constant, A is the surface area of the metal solution boundary, and r is the instantaneous reaction rate. Since current measurements are easily done with modern instrumentation, a peculiar feature of electrochemical techniques is that they provide continuous monitoring of the reaction rate.

Integration of the current over a period of time affords the electrical charge, Q, which can be transformed into the amount of material in moles, N, converted in the electrochemical reaction using Faraday's law:

$$Q = nFN \tag{4}$$

A third quantity of fundamental importance in electrochemistry is the electrode potential, which can be considered as an adjustable driving force for the electrochemical reactions. In general terms, as the potential of an electrode is made more negative, the average energy of the electrons in the metal, which is approximately equal to its Fermi level, becomes higher, giving the electrode more reducing power. Similarly, the oxidizing power of an electrode can be increased by making its potential more positive. While these qualitative arguments are perfectly straightforward, the definition of electrode potentials is complicated by the fact that the potential of a single electrode is not an experimentally measurable quantity. This experimental inaccessibility has given rise to many theoretical attempts to obtain absolute electrode potentials. However, to the authors' knowledge, none of these attempts has gained universal acceptance and, therefore, relative values continue to be the only way in which electrode potentials can be quoted. Simply put, this means that electrode potentials are always measured versus a second, reference electrode, whose value is arbitrarily taken as zero. The potential of the normal hydrogen electrode (NHE) is generally assigned a standard value of zero and serves thus as the primary reference for any other electrodes. For a generalized process involving the transfer of n electrons,

$$Ox + ne \Leftrightarrow Red \tag{5}$$

where *Ox* and *Red* represent the oxidized an reduced partners of the redox couple, the thermodynamic potential, *E*, of the corresponding electrode is given by the well known Nernst equation, which is unquestionably one the most important equations in electrochemistry,

$$E = E^{o} + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}} \tag{6}$$

where E^o is the potential under standard conditions, a_{Ox} and a_{Red} are the activities of the oxidized and reduced species, respectively, and the remaining terms have their usual meaning. Extensive tabulations of standard potential values are available. To avoid the complications associated with the use of thermodynamic activities and activity coefficients, very often activities are replaced by concentrations. In this case, the standard potential is replaced by the formal potential, $E^{o'}$, which is usually dependent on medium conditions since it includes the activity coefficients. Therefore, a more practical version of the Nernst equation is as follows

$$E = E^{o'} + \frac{2.303RT}{nF} \log \frac{[Ox]}{[Red]} \tag{7}$$

The factor 2.303 reflects the replacement of natural by decimal logarithms. At 25°C, 2.303RT/F is equal to the familiar 0.05916V, which every freshman chemistry student ends up committing to memory.

The Nernst equation is a thermodynamic equation and, thus, can only be rigorously applied to equilibrium situations (i=0). In spite of this apparent limitation, eq. 7 is successfully applied when current flows across the electrode in question, as long as the heterogeneous electron transfer process is fast (*reversible* in electrochemical jargon). Under these conditions, the equation is useful to calculate the concentrations at the electrode surface of *Ox* and *Red* that are generated when specific potential values are imposed to the electrode. Fast electron transfer kinetics allows the electrochemical reaction to adapt quickly to the changing potential values on the electrode surface, maintaining a pseudo-equilibrium situation as well as the validity of the Nernst equation. Therefore, the term *nernstian* is also used when describing kinetically fast or reversible electron transfer processes.

Finally, we must point out the potential of a galvanic cell, such as that represented in Fig. 1.1, can always be calculated with the following equation,

$$E_{cell} = E_{cathode} - E_{anode} \tag{8}$$

in which the cathode and anode potentials are obtained individually using eq. 7.

1.2 Mass Transport

Current is simply the movement of ions and/or electrons across conducting media. In electrochemical cells, the movement of charged and neutral species is

fundamentally important. Quite often it is the rate of these movements that determine the potentials and currents measured in the cell. No treatment of electrochemistry can thus overlook mass transport mechanisms. The three relevant mechanisms that may arise in electrochemical cells are migration, convection, and diffusion. In most electrochemical techniques, conditions are chosen so that transport of the electroactive species is affected by a single mechanism, typically diffusion. A brief discussion of each of these modes of mass transport follows.

Migration is the movement of ions under the influence of an electric field. Therefore, uncharged species are not affected by migration. Although migrational movements can be described mathematically, in most voltammetric techniques it is desirable to remove migration contributions to the mass transport of the primary electroactive species, that is, the molecule or ion under study or analysis. This is accomplished by adding a large excess of an easily ionizable salt, which will dissociate to produce a large amount of inert anions and cations. These ions become the migration current carriers, thus releasing the electroactive species (if charged) from migration effects. The ionizable salt used for this purpose is called the *supporting electrolyte.* To be effective, its concentration must be about 100 times higher than that of the electroactive species. A second beneficial effect of the supporting electrolyte is to increase the conductivity of the solution, thus decreasing cell resistance effects that are very detrimental for recording accurate current responses.

Convection is mass transport resulting from movements of the solution as a whole. Convection can be driven by stirring, solution flow, or by movements of the electrodes. In quiet, thermostatted electrochemical cells, convection may arise from density gradients only after rather long experiments. In fact, it is usually the onset of convection that limits the maximum duration of voltammetric or chronoamperometric experiments. In shorter experiments convection is not a factor in mass transport as long as the solution is quiescent and the electrodes are stationary.

Diffusion is mass transport driven by a gradient of chemical potential. Anytime that the concentration of a molecule or ion (charge is of no concern here) is uneven throughout a solution, mass transport will take place to restore the homogeneity of the solution. In other words, transport will proceed from regions of high concentration to regions of low concentration. Diffusional phenomena are very important across many scientific and engineering disciplines. Fortunately, diffusion can be described mathematically, which facilitates the quantitative treatment of many electrochemical phenomena. The rate of diffusion of any chemical species is described by its diffusion coefficient, D, that is usually expressed in units of cm^2/s. Most small organic or inorganic molecules or ions have D values in the vicinity of 10^{-5} cm^2/s. This value decreases with molecular size. For instance, for spherical molecules the Stokes-Einstein equation establishes that

$$D = kT/6\pi\eta a \tag{9}$$

where k is the Boltzmann constant, η is the solution viscosity and a stands for the effective hydrodynamic radius of the diffusing species. This equation also reveals explicitly that D values depend on the temperature and the composition of the solution.

To quantitate one-dimensional diffusion rates the concept of material *flux* is very useful. The diffusional flux, J, is defined as the number of particles crossing a unit surface area perpendicular to the direction of mass transport per unit time. Fick's first law establishes that the flux is directly proportional to the concentration gradient. The proportionality constant is precisely the diffusion coefficient, that is,

$$J = -D \cdot \left(\frac{\partial c}{\partial x} \right) \tag{10}$$

and the negative sign denotes the fact that the material flux moves against the gradient. This equation is extremely useful to calculate currents under conditions of complete conversion, i.e., whenever all the molecules or ions reaching the electrode surface undergo instantaneous electrochemical reaction. In such cases, the flux at the electrode surface is directly proportional to the resulting current.

Fick's second law permits the calculation of concentration changes as a function of time. Its mathematical expression is given below

$$\frac{\partial c}{\partial t} = D \cdot \left(\frac{\partial^2 c}{\partial x^2} \right) \tag{11}$$

Fick's laws provide a complete and detailed description of diffusional mass transport for any species subject to concentration gradients. To find the analytical solutions of the resulting differential equations, appropriate boundary conditions must be provided detailing initial and limiting concentrations and extent of electrochemical conversion at the electrode surface. Some examples will be given in later chapters.

1.3 Kinetics of Electrode Reactions

In most electrochemical experiments we are interested in recording a current-potential curve. For instance, let us assume that we apply an increasingly positive potential to an electrode (or that we make its potential increasingly positive against a reference electrode). The more positive the potential becomes, the more oxidizing power is conferred to the electrode and, at some point, one of the cell components will start to undergo an oxidation reaction. This reaction will translate into current flowing across the cell, a situation that is represented in Fig. 1.2. Notice that this curve is composed of three distinctive regions. In the first region (low potentials), there is no significant current flow, because the potential is not sufficiently positive to drive the oxidation process. In the second region (intermediate potentials), the current increases with the potential, as one

would generally anticipate from simple kinetic arguments. A third region (high potentials) is characterized by the leveling of the current, which reaches a constant or limiting value independent from the potential. This is due to limitations imposed by the finite rate of mass transport that can be achieved in the solution.

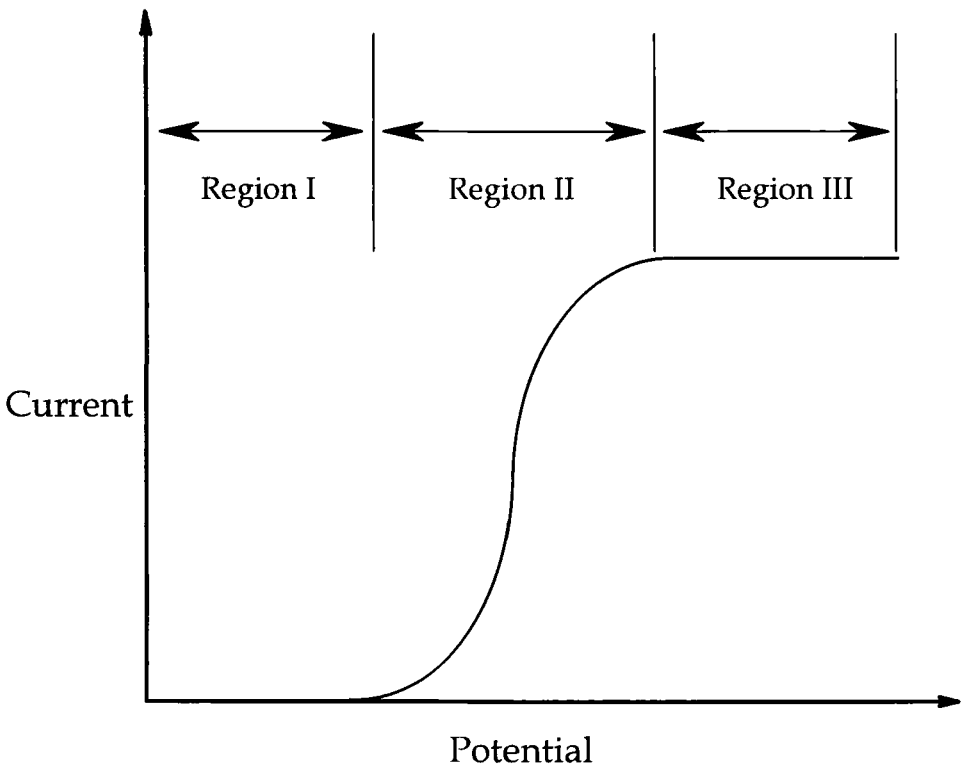

Figure 1.2: Typical current-potential curve.

An electrode reaction is a heterogeneous process that takes place at the interface between the electrode and the solution. Therefore, the overall rate or current depends on the rates of two distinct processes: the actual heterogeneous electron transfer process and the transport of the reactant species from the solution to the electrode surface. The slowest one of the two processes determines the overall current. Fig. 1.2 illustrates this situation clearly. In the intermediate potential region the kinetics of the electrode reaction controls the current level. In this region mass transport is still sufficiently fast to be "transparent", that is, it shows no effect on the overall current. However, at higher potentials, the electrochemical reaction is driven to very fast rates, increasing the demand for electroactive species to an extent that it becomes impossible for mass transport to keep pace. Therefore, a current plateau

develops as the current reaches the maximum limit that mass transport processes can provide. These ideas are mathematically expressed by the simple equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_l} \tag{12}$$

in which i stands for the overall current, i_k is the current that can be obtained at that potential and i_l is the limiting current that can be reached through mass transport. In this section we will describe the potential dependence of the current assuming no limitations from mass transport.

Any theoretical formulation of electrochemical kinetics must reduce to the thermodynamic limit (Nernst equation) when equilibrium is reached. Furthermore, the empirical Tafel equation establishes a mathematical relation between the current and the overpotential η (difference between the applied potential and the corresponding equilibrium potential for the electrode system in question)

$$\eta = a + b \cdot \log i \tag{13}$$

where a and b are constant values characteristic of the system. Let us consider a generalized heterogeneous electron transfer process between species *Ox* and *Red* (see eq. 5). Using eq. 3, we can write for the forward reaction (*Ox*→*Red*)

$$r_f = k_f \cdot C_{Ox}(0,t) = \frac{i_c}{nFA} \tag{14}$$

in which k_f is the rate constant for the forward reaction, i_c is the cathodic current. Notice that the heterogeneous character of the process is manifested by the fact that the reaction rate is directly proportional to the reactant concentration at the electrode surface $C_{Ox}(0,t)$. We can write a similar equation for the reverse or backward process (*Red*→*Ox*)

$$r_b = k_b \cdot C_{Red}(0,t) = \frac{i_a}{nFA} \tag{15}$$

The total current i flowing through the electrode is simply the difference between the cathodic and the anodic currents,

$$i = i_c - i_a = nFA\{k_f \cdot C_{Ox}(0,t) - k_b \cdot C_{Red}(0,t)\} \tag{16}$$

The way this equation is written implies that we have chosen to describe cathodic currents as positive and anodic currents as negative. This is a common, albeit completely arbitrary, choice that we will maintain throughout the book. Notice also that the rate constants have units of cm/s, a reflection of their heterogeneous character, provided that they operate on concentrations expressed in mol/cm^3.

A key distinguishing feature of electrochemistry is that the reaction rates depend on the applied electrode potential. In fact, to further develop eq. 16 we must provide mathematical expressions to describe this dependence. The Butler-Volmer formulation is the most commonly used for this purpose. The corresponding equations are as follows

$$k_f = k^0 \cdot e^{-\alpha nF(E-E^{o'})/RT} \tag{17}$$

and

$$k_b = k^0 \cdot e^{(1-\alpha)nF(E-E^{o'})/RT} \tag{18}$$

where k^0 is the standard rate constant and α is the so-called transfer coefficient.[1] It is possible to derive these equations using several physical models, but we will constrain ourselves here to explore some of the implications of the Butler-Volmer formulation.

At equilibrium ($E=E_{eq}$) the net current is zero. By combining eqs. 16, 17 and 18 we have

$$nFAk^0 C_{Ox}(0,t) \cdot e^{-\alpha nF(E_{eq}-E^{o'})/RT} = nFAk^0 C_{Red}(0,t) \cdot e^{(1-\alpha)F(E_{eq}-E^{o'})/RT} \tag{19}$$

Under equilibrium conditions, the concentrations of *Ox* and *Red* at the electrode surface are identical to those in the bulk solution and, thus, we can write

$$\frac{[Ox]}{[Red]} = e^{nF(E_{eq}-E^{o'})/RT} \tag{20}$$

which is identical to the Nernst equation (eq. 7). The electrochemical equilibrium, as any other type of chemical equilibrium, is not static. In fact, the forward and backward processes take place at equal rates yielding no net current. However, the electrochemical activity at equilibrium can be expressed in terms of the exchange current, i_0, which is identical to the level of cathodic or anodic currrent. For instance,

$$i_0 = i_f = i_b = nFAk^0 e^{-\alpha nF(E_{eq}-E^{o'})/RT} \tag{21}$$

which, after some manipulation, yields

$$i_0 = nFAk^0 [Ox]^{(1-\alpha)} [Red]^{\alpha} \tag{22}$$

The exchange current is directly proportional to the standard rate constant for the heterogeneous electron transfer process. Both parameters are used to express quantitatively the inherent rates of heterogeneous electron transfer reactions.

Outside equilibrium conditions ($\eta \neq 0$) the Butler-Volmer formulation leads to an important equation which is generally valid to describe the kinetics

of electrochemical reactions in the absence of mass transport limitations. Not surprisingly, this equation is commonly referred to as the Butler-Volmer equation and is given as

$$i = i_0 \left[e^{-\alpha nF\eta/RT} - e^{(1-\alpha)nF\eta/RT} \right] \tag{23}$$

The right term in the equation describes the cathodic component (forward reaction) of the current while the left term describes the anodic component (reverse reaction). Of course, the sign of the overpotential determines which one of the two terms will predominate and control the overall current. At negative overpotentials ($E<E_{eq}$) the cathodic term predominates and at positive overpotentials ($E>E_{eq}$) the anodic term controls the total current. The transfer coefficient α is related to the degree of asymmetry in the electron transfer process. Many simple, one-step electrochemical reactions exhibit values of α close to 0.5. Kinetically sluggish processes or multi-step reactions may present transfer coefficients substantially different from 0.5.

The Butler-Volmer equation reduces to Tafel conditions at extreme overpotentials. For instance, if $\eta<<0$, it can readily be shown that

$$i = i_0 e^{-\alpha nF\eta/RT} \tag{24}$$

as the anodic term becomes negligibly small. Taking logarithms on both sides of the equation and rearranging yields

$$\eta = \frac{RT}{\alpha nF} \ln i_0 - \frac{RT}{\alpha nF} \ln i \tag{25}$$

which is identical in form to the empirical Tafel equation (eq. 13). It is also of interest to explore the Butler-Volmer equation under conditions of small overpotentials. Using the fact that for very small values of the exponent (x) the exponential (e^x) can be approximated by $1+x$, it is easy to show that

$$i = -\frac{i_0 nF}{RT} \eta \tag{26}$$

which demonstrates that the current is linearly related to the overpotential in a narrow range of potentials around E_{eq}.

The kinetics of electrode processes has tremendous significance in several technologically important fields. Unfortunately, many electrochemical reductions or oxidations of simple molecules occur via complicated, multi-step mechanisms. This makes their study far more difficult than this short treatment may reflect.

1.4 References

1. Like k^0, α is temperature dependent. See M. T. M. Koper, *J.Phys. Chem B*, **1997**, *101*, 3168-3173.