

# Understanding Electrochemistry: Some Distinctive Concepts

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This article addresses a few basic ideas about electrochemical systems that cause confusion among newcomers. The arguments are developed from the student's general experience with homogeneous chemistry. The chief goal is to synthesize an understanding of the *heterogeneity* of an electrochemical system and a chemical sense for the important electrochemical variables of *potential*, *current*, and *charge*. A fuller treatment begun along similar lines is available elsewhere (1). The points can be made in five simple statements.

## An Electrochemical System Is Not Homogeneous

Newcomers to electrochemistry have had much more experience with *homogeneous* systems than with *heterogeneous* ones. Heterogeneities almost always exist in electrochemical systems. One cannot understand electrochemistry without grasping the locations at which important events occur. There is a good deal of structure to a typical system; Figure 1(a) offers a representation.

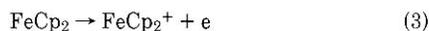
Electrode reactions, such as the evolution of hydrogen,



or the plating of copper,



or the oxidation of ferrocene to ferricenium,



can only take place at the *interface* between the *electrode* and the solution of *electrolyte*. The important point for the moment is that the electrode can only affect or sense the part of the solution in immediate contact with itself. No ferrocene can be oxidized if there is none at the interface, even if it does exist somewhere else in the cell.

Electrode reactions, in fact, tend to make the composition in the nearby solution different from that further away. This effect is shown in Figure 1(b) for an electrode immersed in 1 mM ferrocene in acetonitrile. If reaction (3) takes place at the

interface, the concentration of ferrocene will be drawn down at the surface, as shown in Figure 1(b). Since the normal Brownian motion of molecules tends to homogenize the solution, there is a net *diffusion* of new ferrocene molecules into the depleted zone from more remote regions. Some molecules diffuse all the way to the surface where they undergo reaction (3). Thus, there is a tendency for the system to transport reactants to the electrode from remote points, and the depleted zone widens as the reaction proceeds. If there is stirring,

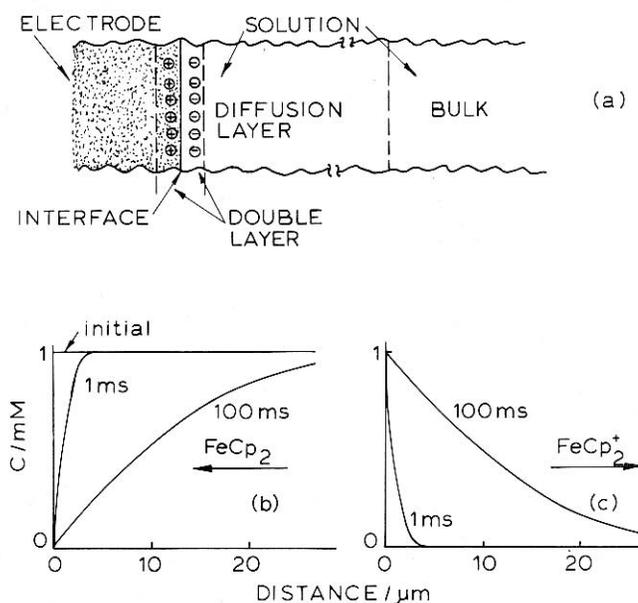


Figure 1. (a) Spatial structure of an electrochemical system. (b) Concentration profiles of ferrocene undergoing oxidation at the electrode. Distance is measured from the electrode toward the bulk. Times are elapsed periods from start of electrolysis. (c) Concentration profiles of ferricenium produced by oxidation of ferrocene.

then the zone widens to a limit, because the stirring keeps the solution homogenized beyond that limit. Just as the electro-reactant is depleted near the interface, the product accumulates nearby, as shown in Figure 1(c). The product gradually diffuses outward from the surface, so its profile also broadens with time. The part of the solution near the electrode, where the composition is affected by an electrode reaction, is called the *diffusion layer*. It is large on a molecular scale, perhaps  $10^4$ – $10^7$  Å, but quite small on the usual dimensions of cells, only  $10^{-4}$ – $10^{-1}$  cm. The *bulk* is the part of the solution, far from the electrode (but still perhaps no more than 0.1 mm away) where the composition is uniform.

Of even smaller dimensions is the structure in the immediate vicinity of the interface. It is intuitive that the part of the solution very near the electrode, within a few molecular layers, must differ in structure from the characteristics of more remote zones, simply because this part of the system is forced to interact with the electrode, which obviously has a very different character from the bulk solvent. Likewise, the distribution of mobile electrons in the part of the electrode in contact with solution must differ from the distribution found in the interior of the metal. These interfacial zones on the two sides of the interface have dimensions of a few tens of angstroms, because that is the scale on which interatomic and intermolecular forces operate. The whole structure is called the *double layer*.

At this point, a very important idea must be grasped. One is taught early to rely on the electroneutrality of chemical phases, i.e., on the idea that positive and negative charges exist in equal numbers within a phase. This is not true of the separate phases which constitute the interface. Usually there are differences, so that phases retain net electrical charges. The differences are small compared to the total number of positive and negative charges present, hence electroneutrality is a very good approximation for most stoichiometric thinking. However, the excess charge has a big effect on the electrical (and electrochemical) properties of a phase.

All conducting phases, such as metals and electrolytes, tend to push the excess charges to their outer boundaries. Thus, the double layer between an electrode and a solution will contain such excesses of charge, as shown in Figure 1(a). If the metal is positively charged, then the solution side has an equal excess of negative ions in the interfacial region. One can show that the whole double layer is electrically neutral, even if both sides are charged.

The excess charge on the metal can be changed at will with a power supply, which is just a pump for electrons. The supply forces electrons to enter or leave the interface until the repulsion of charges remaining there will not allow the supply to remove or add more. The metal can carry positive, zero, or negative charges of continuously tunable magnitude. This feature is the basis for control of potential (see below).

### Many Things Can Happen at Once

An electrode reaction can be rather complicated. Invariably it takes place in a *mechanism* of several steps. Students are familiar with this idea, but it is important to understand that the steps in electrode processes are often very different in *kind*. There is at least one heterogeneous electron-transfer step, like (1), (2), or (3) above. However, there can also be coupled heterogeneous processes of other types, such as (a) adsorption or desorption of precursors, intermediate [e.g., H atoms in (1)] or products, (b) migration of atoms across a surface during electrocrystallization of metals [e.g., Cu in (2)] (c) or surface-mediated recombination of atoms or radicals. There can also be coupled homogeneous reactions in the solution. Acid-base reactions, metal-ligand chemistry, homogeneous redox reactions, and radical-radical recombination processes are quite common. These reactions can precede or follow the heterogeneous electron transfer.

All of these chemical steps are kinetic events, and they all

proceed at rates described by rate constants. The overall rate of the electrode reaction is determined by all of the individual rates together, much as for a mechanism of purely homogeneous steps. The chief differences for electrode reactions are that the heterogeneous steps (a) have *rate constants* that depend on the state of charge of the interface, i.e., the potential of the electrode, and (b) have *rates* that depend on concentration of reactants at the surface.

Since the electrode process can happen only at the electrode, another factor in the overall reaction rate is the rate at which reactants can be brought to the electrode or the rate at which products can be dispersed. *Mass transport* is usefully regarded as part of the overall mechanism, even though it is not a chemical process. Mass transport occurs by *diffusion* (microscopic, random motion), by *convection* (bulk flow, stirring, movement of segments of solution), or by *migration* (movement of ions along an electric field).

As elsewhere in science, one obtains chemical information from a complex electrochemical mechanism by trying to arrange conditions so that a single step, such as mass transfer or heterogeneous electron-transfer, controls the overall rate. It is very often possible to obtain such selective control.

The main message here is that an electrochemical system has a *dynamic* nature of unusual variety. It is essential for a newcomer to obtain a feeling for this aspect as early as possible.

### Current is an Expression of Rate

Figure 2 is a schematic representation of the chemistry in a cell. Usually we focus attention on a single electrode, called the *working electrode*. Suppose ferrocene is being oxidized there according to step (3). Each molecule that is oxidized gives up one electron to the working electrode. These electrons will not be allowed to be separated permanently from the solution on any stoichiometric scale, because huge potential differences would be produced. Instead, the electron will pass through the external circuit and back into the solution at a second electrode called the *counter electrode*. Since the power supply will force the electrons onto species in the solution at the counter electrode, reduction takes place there to an extent equal to the oxidation of ferrocene at the working electrode.

Electrons at either electrode can flow into the electrode or out of the electrode by way of the external circuit. That is, the current can be *reducing* or *oxidizing*, i.e., *cathodic* or *anodic*. However, a current at the working electrode is compensated exactly at the counter electrode. Anodic current at the working electrode implies cathodic current at the counter electrode, and vice versa.

Since electrons are used or supplied on an *integral, stoichiometric basis* in electrode reactions, the flow of electrons at an electrode is directly proportional to the rate of reaction there.

### Potential is an Expression of Electron Energy

The idea of potential is endlessly confused because teachers rely too much on formalism and "convention" in discussions of it. Students never really understand what potential is, in a physical sense, or how it can be manipulated experimentally. The best starting point is the definition from physics (2) that potential is the work required to bring a unit test charge from infinite distance to a point of interest, such as inside a working electrode. It is obvious that the potential of an electrode depends on any excess charge that exists on the electrode. It is also clear that the energy required to add or subtract an electron from the electrode can also be expressed in terms of this potential. The linkage between potential, electron energy, and excess charge on the electrode is the key to an understanding of potential as a chemical variable.

An external power supply, like that in Figure 2, can force extra electrons into or out of the metal side of the double layer

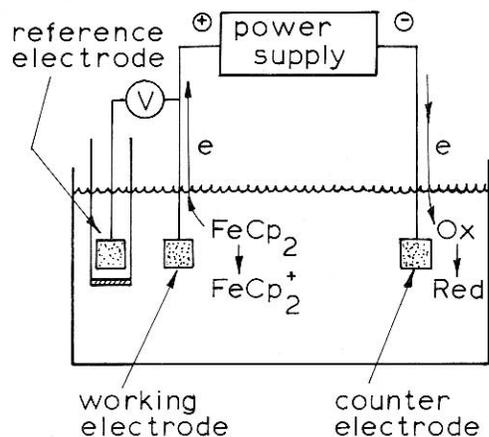


Figure 2. Structure of an electrochemical cell. The voltmeter has a high impedance, so current does not flow in the circuit between the working and reference electrodes.

until its driving force is counterbalanced by the repulsions between the excess charges. With a large excess of negative charges, the potential is very negative and the energy of electrons on the electrode is high. Likewise, a large excess of positive charge implies a very positive potential and low electron energy. By changing the voltage on the power supply, the excess charge, the potential, and the electron energy can be tuned continuously over a wide range.

With this idea in mind, it is easy to understand oxidation and reduction at the electrode. Consider a Pt electrode in contact with a solution of ferrocene in acetonitrile. Ferrocene has the property of being fairly easy to oxidize, i.e., it gives up an electron readily. The energy of the highest electron in the ferrocene molecule is, of course, determined by the molecular structure of ferrocene, and it has the same value for all ferrocene molecules. This highest electron can be lost to an electrode only if the electrode offers a lower energy to the electron, that is, only if the potential is sufficiently positive. The system can be usefully pictured as in Figure 3, where potential and energy of electrons on the electrode run vertically. There is a well-defined energy (potential) where oxidation becomes possible. The *standard potential* for the ferrocene/ferricenium couple is essentially that critical energy. At more negative potentials than  $E^\circ$ , ferricenium would be reduced at the electrode by the relatively high-energy electrons present there.

Any electrode process is characterized by its own standard potential  $E^\circ$ . On the positive side of  $E^\circ$ , the oxidized form of the couple is stable at the electrode, and the reduced form tends to undergo oxidation if it reaches the electrode. Likewise, the zone of potential more negative than  $E^\circ$  is a region where the reduced form is stable and the oxidized form tends to be reduced. Actually, in a zone about 100 mV wide centered on  $E^\circ$ , statistical equilibrium of electrons on the electrode and on species in the solution permits mixtures of oxidized and reduced forms with appreciable amounts of both species.

These ideas can tell us what *may* be possible at a given energy, but the kinetics of the reactions determine whether an energetically allowed reaction actually does occur. Some reactions, such as (1) on Hg, are very sluggish and do not occur at appreciable rates unless a large excess potential beyond  $E^\circ$  is applied. Others, like (3), are quite fast.

Experimentally, one can measure only differences in potentials between two electrodes, so the word *potential* in electrochemical usage means the voltage difference (Fig. 2) between a working electrode and an independent *reference electrode*. The reference electrode is usually arranged, so that it does not pass current and is at equilibrium. It is constructed

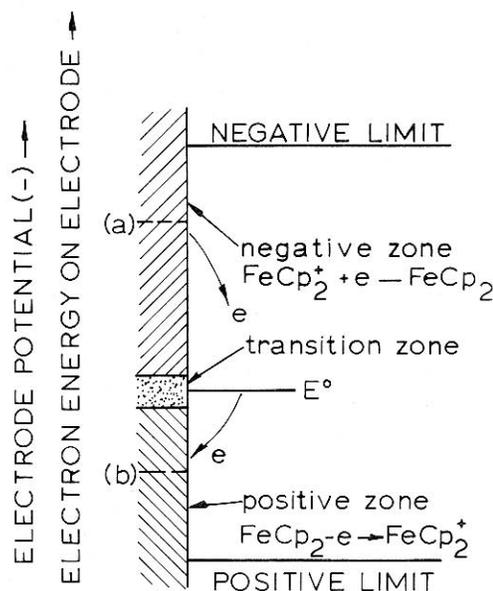


Figure 3. Illustration of potential as an expression of electron energy. At potential (a) ferricenium at the surface would be reduced to ferrocene. At potential (b) ferrocene at the surface is oxidized to ferricenium. The potential limits correspond to values for which the solvent, supporting electrolyte, or electrode material are oxidized or reduced.

so that it contains both forms of a redox couple (e.g.,  $H^+/H_2$ ,  $Hg/Hg_2Cl_2$ ,  $Ag/AgCl$ ) at fixed composition. Electron energies in the metallic part of the electrode are, therefore, fixed at a value near that corresponding to  $E^\circ$  for the couple. This arrangement provides an invariant reference point against which working electrodes can be measured.

Space is too limited here to discuss the manner in which an electrode at open circuit senses the composition of a solution by providing a characteristic potential given by the Nernst equation. However, it is useful for students to understand the process. A discussion is available elsewhere (1). Likewise we cannot discuss the confusing matter of using potentials to extract thermodynamic information (e.g., free energies or equilibrium constants) for chemical reactions. Careful discussions are available in the literature (3, 4).

### One Cannot Control Both Current and Potential Simultaneously

Once the energy available to a reaction has been determined in any chemical system, the reaction proceeds at a rate corresponding to that energy. In homogeneous kinetics, one can dictate the temperature and accept the rate, or one can dictate the rate and accept the corresponding temperature. Likewise in electrochemical systems one can set the potential of an electrode and accept the corresponding current flow, or vice versa. Choosing one variable for control precludes any separate influence over the other.

The five major concepts discussed above give only a foundation for an understanding of electrochemistry. However, experience has shown that they do provide a sound basis for the development of a contemporary working knowledge of the subject.

### Literature Cited

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