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# Potentially Confusing: Potentials in Electrochemistry

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A *potential* quantifies the capacity of a system to do work. A simple example is from mechanics: by lifting a weight, its potential energy increases. When the weight is dropped, that potential energy is converted into kinetic energy. Applying the concept of potential to electrochemical systems can be surprisingly confusing.[1−4] Table 1 shows some "potentials" used in electrochemistry and their different units.[5]

To start, let us consider a voltage measured with a voltmeter for a given system. Analog voltmeters operate by passing a small current through a calibrated resistor and wire coil, generating a small magnetic field, and thus deflecting a needle attached to a fixed magnet. The current passed through the resistor, which causes needle deflection, is proportional to the voltage. This voltage, however, is not the *electric potential* difference of the system. Electric potential $\phi$ is the line integral of the electric field $\vec{E}$ along a path from a reference point (often at infinite distance from the system) to a given position:

$$\phi = -\int_{\text{path}} \vec{E} \cdot \mathrm{d}l \tag{1}$$

Electric fields are generated by (uncompensated) electric charge. Thus, $q \cdot \phi$ is a measure only of the electric component of the work needed to move a test charge $q$ from a reference position to the position of interest in the system. If the charge moves through different phases, *i.e.*, across interfaces of different materials, the electric work does not fully account for the total work.

Consider two metals with different work functions (*i.e.*, the energy required to remove an electron from the metal to vacuum), *e.g.*, Au and Ti. If Ti and Au are put in contact, initially electrons transfer from Ti to Au, generating an interfacial electric field and thus an electric potential difference across the interface. Yet if you connect a voltmeter with one lead to Ti and the other to Au, you measure 0 V. *A voltmeter does not only measure the electric potential difference between the two points in the system.*

A voltmeter measures the difference in the electrochemical potential of electrons ($\bar{\mu}_e$), because it is this difference that drives the current through the voltmeter needed to make the measurement.[6] The electrochemical potential for electrons is also the Fermi level. In general, it is the gradient (*i.e.*, derivative with respect to position, usually per cm) in $\bar{\mu}$ that

causes transport. The flux ($\mathbf{J}$) of species $j$ (usually in mol·cm$^{-2}$·s$^{-1}$) is given by:

$$\mathbf{J}_j = -\left(\frac{C_j D_j}{RT}\right)\nabla\bar{\mu}_j \tag{2}$$

The terms $C_j$ and $D_j$ are the concentration and diffusion coefficients for the species $j$ (e.g., in units of mol·cm$^{-3}$ and cm$^2$·s$^{-1}$, respectively), and $\nabla\bar{\mu}_j$ is the spatial gradient in the electrochemical potential—*the underlying driving force for transport*. $R$ is the gas constant, and $T$ is temperature. Chemical reactions can occur throughout the system and progress in their thermodynamically favorable direction to minimize free energy. When $\nabla\bar{\mu}_j = 0$ and $\frac{\partial\bar{\mu}_j}{\partial t} = 0$ for all species $j$ and everywhere in a system, the system is at electrochemical equilibrium (*i.e.*, the system cannot lower its total free energy via the net movement of any species—electrons, ions, or molecules—to another part of the system or via a chemical reaction). Equation 2 governs transport by drift/migration (movement of charged particles in the presence of an electric field), diffusion (movement due to a concentration gradient), and less-common processes (for example, due to spatially dependent activity coefficients). Equation 2 also yields the common "drift-diffusion equation".

The electrochemical potential for species $j$ can be conceptually decomposed:[7]

$$\bar{\mu}_j^{\alpha} = \mu_j^{\alpha} + z_j F\phi^{\alpha} \tag{3}$$

The term $\mu_j^{\alpha}$ is the chemical potential of $j$, relative to a reference state, and $z_j F\phi^{\alpha}$ is the electrostatic energy per mole of $j$ in phase $\alpha$, relative to a reference state. The term $z_j$ is the signed charge number of $j$ (e.g., +1, −1, +2, −2), and $F$ is the Faraday constant (96 485 C·mol$^{-1}$). The chemical-potential-term $\mu_j^{\alpha}$ is the partial molar Gibbs free energy, ignoring electrostatic contributions. It is defined as the derivative (at constant temperature, $T$, and pressure, $P$, and concentration
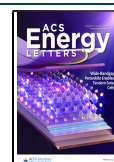
**Table 1. Potentials in Electrochemistry**

| term | symbol | unit | brief definition | significance/example of use |
|------|--------|------|------------------|------------------------------|
| electrochemical potential | $\bar{\mu}_j^\alpha$ | J/mol | partial molar Gibbs free energy of a given species $j$ in phase $\alpha$ | defines criteria for equilibrium; differences in $\bar{\mu}_j^\alpha$ drive the transport, transfer, and reactivity of both charged and uncharged species |
| chemical potential | $\mu_j^\alpha$ | J/mol | partial molar free energy of a given species $j$ in phase $\alpha$ neglecting electrostatic contributions[a] | differences in $\mu_j^\alpha$ describe driving force for reactions between uncharged species and the direction of diffusive transport |
| electric potential | $\phi$ | V | electric work needed to move a test charge to a specific point in space from a reference point (often at infinite distance) divided by the value of the charge | defines direction of electron transport in metals; gradient gives electric field; used to calculate electric potential energy |
| electrode potential | $E_{we}$ | V | free-energy change divided by the electron charge associated with moving an electron (and any associated ion/solvent movement/rearrangement) from a reference state (often a reference electrode) to the working electrode | indicates oxidizing or reducing power of an electrode; related to the Fermi level of electrons in electrode |
| solution potential | $E_{sol}$ | V | free-energy change divided by the electron charge associated with moving an electron (and any associated ion/solvent movement/rearrangement) from a reference state (often a reference electrode) into the bulk of a solution via a redox reaction | indicates oxidizing or reducing power of electrons involved in electrochemical redox equilibria; related to "Fermi level" of the electrons in solution and equivalent to the solution reduction potential |
| overpotential | $\eta$ | V | generally, the difference between the applied electrode potential and the electrode potential when in equilibrium with the target electrochemical reaction | $\eta \cdot F$ gives the heat released, above that required by thermodynamics, per mole of electrons to drive an electrochemical process at a given rate; $F = 96485$ C·mol$^{-1}$ |

[a]That is, no "long-range" electrostatic interactions due to uncompensated charge, as would be described by the Poisson equation in classical electrostatics. The electrostatic terms that describe electron–nucleus and electron–electron interactions and dictate Coulombic potentials in the Schrödinger equation are included.

of all other species, $n_{i \neq j}$) of the Gibbs free energy with respect to the number of particles (in the phase in question):

$$\mu_j^\alpha = (\partial G_{int}/\partial n_j)_{T,P,n_{i \neq j}} \tag{4}$$

The term $G_{int}$ is the chemical free energy neglecting contributions from "long-range" electrostatic effects, and $n_j$ is the number of moles of species $j$. In a mixture, the chemical potential is determined as a function of the activity, $a_j^\alpha$, and referenced to the chemical potential at standard state, $\mu_j^o$.

$$\mu_j^\alpha = \mu_j^o + RT \ln a_j^\alpha \tag{5}$$

The term $a_j^\alpha = \gamma_j^\alpha C_j^\alpha / C_j^{o,\alpha}$, where $\gamma_j^\alpha$ is the activity coefficient, a factor that allows the use of ideal thermodynamic equations with concentrations $C_j^\alpha$ and $C_j^{o,\alpha}$ as inputs. The term $C_j^{o,\alpha}$ is a reference concentration, usually taken to be 1 M for soluble species. The term $\mu_j^o$ is determined relative to a reference state (e.g., $\mu_{H^+}^o \equiv 0$ at 25 °C in water). The activity term takes into account that the chemical potential increases with concentration. In physics, the electrochemical potential is often not defined explicitly, instead the electrostatic energy $z_j F \phi^\alpha$ is included directly in the "chemical potential", and an *intrinsic or internal chemical potential* without long-range electrostatic effects is defined as a new quantity.[7]

The fact that gradients in electrochemical potential, not electric potential, drive charge flow explains why a voltmeter cannot measure the electric potential between two metals, *i.e.*, above $\bar{\mu}_e^{Ti} = \bar{\mu}_e^{Au}$ but $\phi^{Ti} \neq \phi^{Au}$. A voltmeter measures $\Delta\phi$ between two points in a system only if they have a *common* chemical potential. Consider a metal wire acting as a resistor. The concentration of electrons is large, $\sim 10^{22}$ cm$^{-3}$, and the density of electronic states at the Fermi level is high. Thus, even when current flows the chemical potential of electrons is invariant across the length of the wire. Thus, for two different locations $\alpha$ and $\beta$ in the same metal

$$\Delta\bar{\mu}_e = \bar{\mu}_e^\alpha - \bar{\mu}_e^\beta = \mu_e^\alpha - F\phi^\alpha - \mu_e^\beta + F\phi^\beta = -F\Delta\phi \tag{6}$$

A voltmeter thus measures $\frac{-\Delta\bar{\mu}_e}{F} = \Delta\phi$ between two points in a common metallic phase. By definition, electrons flow to regions of more-negative $\bar{\mu}_e$ (to lower their free energy), but to more-positive $\phi$. Under this condition, eq 2 simplifies to a form of Ohm's law. *The foregoing discussion emphasizes that all measurements of potential are necessarily measurements of electrochemical potential and any inferences about electric potential require one or more assumptions.*

Now let us consider the term electrode potential, $E_{we}$, in the context of these other potentials (the "we" refers to the working electrode). The electrode potential, with units of V, is given by the difference in $\bar{\mu}_e$ per charge, in the working electrode, relative to $\bar{\mu}_e$ in a second electrode that is typically set via a reversible electrochemical half reaction (*i.e.*, a reference electrode, indicated by "re"):

$$E_{we}(\text{vs } E_{re}) = \frac{-(\bar{\mu}_e^{we} - \bar{\mu}_e^{re})}{F} \tag{7}$$

The sign convention is again consistent with electrons spontaneously flowing toward more-positive $E_{we}$. Practically, one measures the voltage difference between the working and reference electrodes. Because $E_{we}$ and $E_{re}$ are each themselves defined relative to an arbitrary reference (that cancel in the
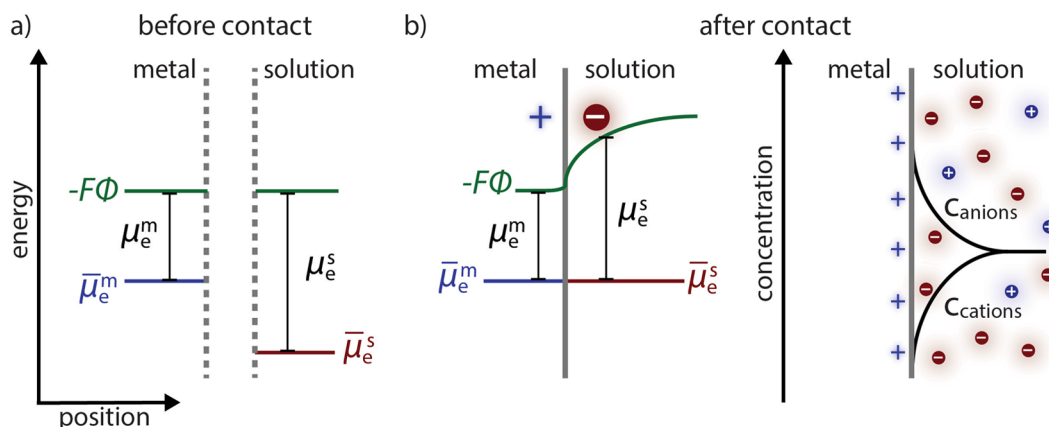
**Figure 1.** Electrochemical equilibrium at an electrode-electrolyte interface. (a) Initially, the electrochemical potential of the electrons is different in the metal electrode and solution. (b) Once the two phases are brought into contact, electrons are driven by the gradient in electrochemical potential across the interface. This process leads to the addition of positive charge on the metal surface that is balanced by negative ions in the solution (the so-called double layer). The ionic charge in the solution matches the charge on the metal due to overall charge neutrality. This is analogous to processes that occur to form electric potential differences ($\Delta\phi$) as space-charge regions at semiconductor interfaces and as Donnan potentials at membrane-electrolyte interfaces. The absolute charge of the metal surface ($\sigma^m$) will also depend on the potential of zero charge ($E_{\sigma=0}$) of the specific electrode material in the given electrolyte. Even in the absence of electron transfer across the interface, most electrode surfaces carry surface charge due to adsorption of electrolyte ions or ionization of surface-functional groups that induces changes in $\sigma^m$. $E_{\sigma=0}$ is the applied potential where $\sigma^m = 0$. The equilibration process described in this figure leads to a change in $\sigma^m$, although the ultimate sign and magnitude of $\sigma^m$ depends on $E_{\sigma=0}$ and the redox species.

difference), the cell voltage is usually written $E_{cell} = E_{we} - E_{re}$. The open-circuit (oc) cell voltage is related to the Gibbs free-energy change of the *overall* electrochemical reaction occurring at the working and reference electrodes:

$$E_{cell,oc} = \frac{-\Delta G_{rxn}}{nF} \qquad (8)$$

Electrode potentials can also be measured during spontaneous electrochemical reactions (like corrosion) or can be controlled by a potentiostat in a conventional three-electrode experiment. While eq 7 focuses on $\bar{\mu}_e$, it is important to note that these $\bar{\mu}_e$ are coupled to $\bar{\mu}_j$ of other species, for example ions, via chemical reactions.[8]

Now let us consider three simple electrochemical systems where the conceptual framework of partitioning $\bar{\mu}_j^\alpha$ into chemical and electric components is useful.

**Example 1**: **The electrochemical double layer and the solution potential/Fermi level**. Consider a metal electrode in equilibrium with a redox couple (at say 10 mM) with both the oxidized (O) and reduced (R) form present dissolved in an inert electrolyte (Figure 1). Intuitively, we know that the electron "energy" in the solution must equilibrate with $\bar{\mu}_e$ (the Fermi level) in the electrode. But how precisely does this occur? We can write the electrochemical reaction as

$$O + ne \rightleftharpoons R \qquad (9)$$

where $e$ is an electron *residing in the metal electrode*. At equilibrium, the sum of $\bar{\mu}_j^\alpha$ for products must be equal to that for reactants. This is true for any process that has a sufficient rate to be considered at equilibrium over the relevant time scale. We can therefore relate $\bar{\mu}_e$ in the metal to $\bar{\mu}$ for O and R in solution and define a solution Fermi-level (even though there are practically no "free" electrons in the solution).[9]

$$\bar{\mu}_e^m = \frac{\bar{\mu}_R^s - \bar{\mu}_O^s}{n} \equiv \bar{\mu}_e^s \qquad (10)$$

Typically, the standard hydrogen electrode (SHE) is defined as the reference state. A Pt electrode in equilibrium with $H_2$ and $H^+$ (at unit activity) thus has $\bar{\mu}_e^{Pt} = 0$ because $\bar{\mu}_{H_2}^s - \bar{\mu}_{H^+}^s = 0$ under this (arbitrary) definition.

Since electrochemical potentials and reduction potentials are both referenced to a standard state, we can explore the meaning of $E_{sol}$. From the definition of the electrochemical potential:

$$\frac{-\bar{\mu}_e^s}{F} = -\left( \frac{\bar{\mu}_R^s - \bar{\mu}_O^s}{nF} \right) = -\left( \frac{\mu_R^o}{nF} + \frac{RT}{nF}\ln a_R^s + \frac{z_R}{n}\phi^s \right.$$
$$\left. - \frac{\mu_O^o}{nF} - \frac{RT}{nF}\ln a_O^s - \frac{z_O}{n}\phi^s \right) = E_{O/R}^o - \frac{RT}{nF}\ln a_R^s / a_O^s$$
$$- \phi^s = E_{sol} \qquad (11)$$

The solution potential, $E_{sol}$ (in V), is thus given by the Nernst equation (with the addition of the $-\phi^s$ term that depends on the electric potential reference state and cancels when measured versus a reference electrode at the same $\phi^s$) and directly related to the solution Fermi level. As a caveat, it is important to remember that, practically, $E_{sol}$ can be difficult to measure because of slow electrochemical kinetics. As an example, consider an electrolyte containing water and dissolved $O_2$; $E_{O_2/H_2O}$ cannot be measured with a metal electrode because other undefined electrochemical processes set $E_{we}$ as opposed to equilibration with the kinetically slow oxygen couple (the species with the largest exchange current dominates the measured electrode potential).

Let us now return to the concept of electrochemical equilibration. Upon contact, the initial difference in $\bar{\mu}_e$ drives charge transfer across the electrode/electrolyte interface, leading to an interfacial *electric* potential drop that affects $\bar{\mu}_e^m$ relative to $\bar{\mu}_e^s$ until they are equal. The amount of charge that must be transferred to reach equilibrium depends on the capacitance of the electrode but is generally small compared to the number of electrons in the metal and redox species in
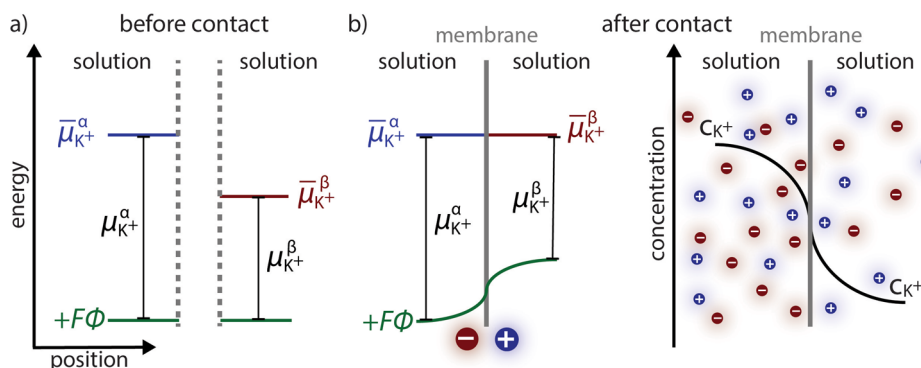
**Figure 2.** Establishing electrochemical equilibrium across a perfectly cation-selective membrane. (a) The two adjacent phases, varying in KCl concentration, have different $\bar{\mu}_{K^+}$ before coming into contact. The $Cl^-$ ions in this example do not equilibrate across the interface because the membrane is assumed to completely exclude them. (b) Upon contact, $K^+$ transports from left to right according to $\nabla \bar{\mu}_{K^+}$, i.e., until equilibrium is reached and $\bar{\mu}_{K^+}^\alpha = \bar{\mu}_{K^+}^\beta$. As $Cl^-$ cannot transport, space-charge regions are formed that result in an electric potential gradient and a position-dependent $a_{K^+}$ on both sides of the membrane.
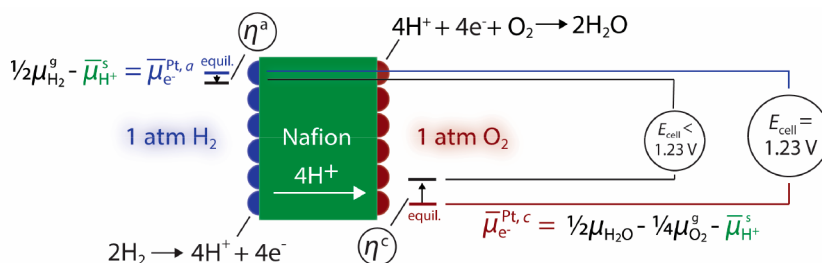


**Figure 3.** Electrochemical potentials in a fuel cell. In equilibrium, $\bar{\mu}_{e^-}^{Pt}$ match with the electrochemical potentials of the other reaction partners at the cathodic and anodic triple-phase boundaries (according to stoichiometry). When a fuel cell is operated at a cell potential $E_{cell} < 1.23$ V the free energy stored in the adjacent 1 atm $H_2$ and $O_2$ compartments is released to do work in the external circuit. Current-density-dependent overpotentials develop at the anode and cathode which are associated with kinetic limitations at the catalyst sites, leading to a free-energy loss, as heat, compared to the theoretical value of 1.23 V.

the electrolyte (so that the bulk activity and thus $\mu$ for all the species is practically unchanged). The extra charge on the metal−electrode surface is compensated by ionic charge in the electrolyte. The concentration of the compensating ions decreases with distance from the electrode (as given by the Poisson-Boltzmann distribution) such that, at equilibrium, $\bar{\mu}_j$ *for all species are constant with position*, through the double layer, and into the bulk electrolyte.

**Example 2: Semipermeable membranes and membrane potentials**. Consider a membrane that is selective for the transport of cations, *e.g.*, an ionomer or a biological membrane. Imagine the membrane separating two compartments containing, for example, aqueous KCl at different concentrations (Figure 2). How do the chemical, electric, and electrochemical potentials change in moving across the membrane from one compartment to the other at equilibrium? Let us assume perfect permselectivity, meaning only the cations can be moved and equilibrated across the membrane (the rate of anion equilibration is negligible). At equilibrium, the electrochemical potential of $K^+$ must be constant across the entire system. Labeling points far from the interface in the two compartments $\alpha$ and $\beta$ yields

$$\bar{\mu}_{K^+}^\alpha = \mu_{K^+}^\circ + RT \ln a_{K^+}^\alpha + F\phi^\alpha = \mu_{K^+}^\circ + RT \ln a_{K^+}^\beta + F\phi^\beta = \bar{\mu}_{K^+}^\beta$$

$$\phi^\alpha - \phi^\beta = \frac{RT}{F}\ln a_{K^+}^\beta/a_{K^+}^\alpha \qquad (12)$$

Because $a_{K^+}^\beta \neq a_{K^+}^\alpha$, $K^+$ flows from one compartment to the other to reach equilibrium, *i.e.* when $\bar{\mu}_{K^+}^\alpha = \bar{\mu}_{K^+}^\beta$, resulting in a charge imbalance and thus electric potential difference $\phi^\alpha -$

$\phi^\beta$ across the membrane. As the membrane was assumed to block $Cl^-$ transport, there is no way for $\bar{\mu}_{Cl^-}$ to equilibrate, and $\bar{\mu}_{Cl^-}^\alpha \neq \bar{\mu}_{Cl^-}^\beta$. This electric potential difference is known as a Donnan potential and found in biological cells and various electrochemical devices.[7]

It is instructive to consider how membrane *electric* potentials are experimentally determined. Usually two identical reference electrodes are placed on either side of the membrane, and the membrane potential, $\phi^\alpha - \phi^\beta$, is taken as the measured voltage difference. But if voltmeters measure differences in $\bar{\mu}_e$, and not electric potential differences, how can this be? The electrons in the reference-electrode wire are in equilibrium with electrons involved in the reference-electrode half reaction, *e.g.*, $AgCl + e^-(Ag) \rightleftharpoons Ag + Cl^-(aq)$, such that

$$\bar{\mu}_{e^-}^{Ag} = \bar{\mu}_{Ag}^{Ag} + \bar{\mu}_{Cl^-}^s - \bar{\mu}_{AgCl}^{AgCl} \qquad (13)$$

The activity of $Cl^-$ is the same in the two reference electrodes, and we neglect junction potentials across the frits used to separate each reference electrode from each test solution (which are small if both contain electrolytes at high concentrations). The membrane potential affects the value of $\bar{\mu}_{Cl^-}^s$ and thus also $\bar{\mu}_{e^-}^{Ag}$ between the two Ag wires. A voltage is measured because $Cl^-$ ions and electrons in the reference electrodes are not in equilibrium ($\bar{\mu}_{Cl^-}^{s,re1} \neq \bar{\mu}_{Cl^-}^{s,re2}$ and $\bar{\mu}_{e^-}^{re1} \neq \bar{\mu}_{e^-}^{re2}$). Because the voltmeter provides a high-impedance path for electronic current, the rate at which equilibrium is

approached is slow enough to not perturb the measurement of the membrane potential.

**Example 3: A fuel cell.** Electrochemical energy-conversion devices such as batteries and fuel cells convert between chemical and electrical energy. Consider a proton exchange membrane (PEM) fuel cell with a Nafion membrane, Pt hydrogen oxidation reaction (HOR) catalyst, and Pt oxygen reduction reaction (ORR) catalyst (Figure 3). $O_2$ gas at 1 atm is flowed over the cathode, and $H_2$ gas at 1 atm is flowed over the anode. First, let us consider open circuit when negligible net current is flowing through the external circuit (*e.g.*, during measurement with a high-impedance voltmeter). Because there is negligible flux, the electrochemical potential of $H^+$ in the Nafion, $\bar{\mu}_{H^+}^s$, is constant through the phase. Electric fields exist only at the interfaces between Nafion and the Pt catalysts and extend only a few nanometers into Nafion (*i.e.*, the Debye screening length), because the $H^+$ are mobile and concentrated in Nafion. The chemical potential $\mu_{H^+}^s$ is thus also constant through the membrane (except at the interfaces where double layers form and $\mu_{H^+}^s$ is spatially varying to give constant $\bar{\mu}_{H^+}^s$).

Now consider the Pt catalyst/electrodes. If zero net current is flowing, does that mean $\bar{\mu}_e$ values at the Pt anode and cathode are the same? No. The electrons in the Pt anode (a) are in equilibrium (in the absence of net current flow) with the $H_2(g)$ and $H^+$ in Nafion, governed by

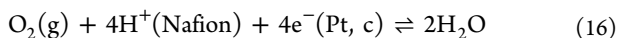$$4H^+(\text{Nafion}) + 4e^-(\text{Pt, a}) \rightleftharpoons 2H_2(g) \tag{14}$$
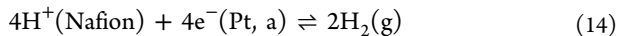
We write the electrochemical potential equality that is required under no current flow:

$$\bar{\mu}_{e^-}^{\text{Pt,a}} = \frac{1}{2}\bar{\mu}_{H_2}^g - \bar{\mu}_{H^+}^s \approx 0 \text{ kJ/mol} \tag{15}$$

The value of $\bar{\mu}_{e^-}^{\text{Pt,a}}$ is ~0 because of the standard states chosen ($\bar{\mu}_{H^+}^o = \mu_{H_2}^o = 0$) and is arbitrary.

At the Pt cathode (c), $\bar{\mu}_{e^-}^{\text{Pt,c}}$ is governed by the equation

$$O_2(g) + 4H^+(\text{Nafion}) + 4e^-(\text{Pt, c}) \rightleftharpoons 2H_2O \tag{16}$$

In the absence of current, we then have

$$\bar{\mu}_{e^-}^{\text{Pt,c}} = \frac{1}{2}\bar{\mu}_{H_2O}^s - \frac{1}{4}\bar{\mu}_{O_2}^g - \bar{\mu}_{H^+}^s \approx -119 \text{ kJ/mol} \tag{17}$$

Both $\bar{\mu}_{O_2}^g$ and $\bar{\mu}_{H^+}^s$ would be (arbitrarily) defined as zero if $O_2$ and $H^+$ are in their standard states, the temperature is 25 °C, and electrostatic potential is defined as zero in the solution. The open-circuit cell potential can then be calculated:

$$\bar{\mu}_{e^-}^{\text{Pt,c}} - \bar{\mu}_{e^-}^{\text{Pt,a}} = \frac{\Delta G_{\text{rxn}}}{n} = -FE_{\text{cell,oc}} \tag{18}$$

This yields $E_{\text{cell,oc}} = 1.23$ V, the thermodynamic voltage for water electrolysis under standard conditions. $E_{\text{cell,oc}}$ is also known as the electromotive force or *emf* of a battery or fuel cell. The system thus could be considered out of equilibrium in this state because the $O_2$ and $H_2$ on either side of the cell cannot mix across the Nafion membrane and react, and electrons cannot exchange between electrodes at open-circuit.

During operation, when ionic and electronic current flow in the fuel cell, there must be gradients in $\bar{\mu}_j^\alpha$. In the Nafion membrane there is a gradient in $\bar{\mu}_{H^+}^s$, but, as in the case of the metal wire, the high concentration of $H^+$ means that changes to $a_{H^+}^s$ are negligible and the spatial dependence of $\bar{\mu}_{H^+}^s$ is largely due to a gradient in electric potential $\phi^s$. The current

can thus be described as migration or drift in the Nafion, and losses (*overpotentials*) are ohmic and generally increase linearly with current. In the Pt-catalyst and electrode structures, electron current flows, which leads to small gradients in $\bar{\mu}_e^{\text{Pt}}$ (particularly in the catalyst layer where electronic connectivity between Pt particles and carbon support is often nonideal). The largest loss in free-energy driving force occurs at the Pt/Nafion interfaces because of the slow kinetics of the ORR (and to a lesser extent HOR). The total free energy extractable from a fuel cell is thus never ideal under current flow; output voltages are always less than 1.23 V.

More generally, an overpotential is the free energy used to drive an electrochemical reaction away from equilibrium. Including kinetic, transport, and other contributions, the overpotential is

$$\eta = E_{\text{app}} - E_{\text{rev}} \tag{19}$$

where $E_{\text{app}}$ is the electrode potential applied, for example by a potentiostat, relative to a defined reference, and $E_{\text{rev}}$ is the reversible potential of the redox reaction (*i.e.*, the potential of a hypothetical nonpolarizable electrode driving the desired reaction with no overpotential under the given conditions) relative to the same (arbitrary) reference. We note that because of mass-transport limitations, $E_{\text{sol}}$ can be position-dependent while $E_{\text{rev}}$ is not (as it is defined under equilibrium conditions). For this reason, the kinetic component of the overpotential, $\eta_k$, is the difference between the electrode and solution potentials (as defined in Table 1) across the electrode interface over the relevant distance where electron/ion-transfer takes place (thus avoiding convolution with mass-transport and ohmic losses). It is this kinetic overpotential that practitioners are generally referring to when discussing electrocatalyst performance, although it is often difficult to completely remove the influence of other overpotential contributions (*e.g.*, from electronic and ionic transport).

*Summary.* Fundamentally, there are several key points we hope the reader will internalize and use when considering any electrochemical system to avoid confusion regarding potentials:

- Measurements of potential differences are necessarily of the total free-energy difference. Decomposing this total into differences in activity, electric potential, and other terms (as needed to describe all the relevant contributions to the free energy) therefore requires a model and assumptions.

- Transport of any species is governed by the spatial gradient in the electrochemical potential. Generally, knowledge of the electric field alone (*i.e.*, the gradient in the electric potential) is insufficient to understand the transport of charged species except in special cases.

- At equilibrium, the electrochemical potential of any given species must be the same throughout the system, and for any chemical reaction, the sum of the electrochemical potentials of the reactants must equal those of the products. Processes with slow kinetics are, in practical systems, typically ignored in the thermodynamic equilibrium analysis.

- The use of the word "potential" alone should be avoided unless the type of potential is made clear. In electrochemistry, "potential" is usually implied to mean

the electrochemical potential of electrons. When the electric potential or chemical potential is meant, that should be indicated explicitly. Practitioners should also indicate what species and phase are being referred to.

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(7) It is important to further recognize that the electrochemical potential formulation given here is but one model that can be used to describe the total free energy of a given species. Electric potential gradients exist in all molecules because of the nuclei and electrons. The separation of electric energies into "long-range" ($zF\phi^\alpha$) and "short-range" ($\mu^\alpha$) components is particularly useful in electrochemical systems where (long-range) interfacial electric fields can be controlled between and across phases, but it is not otherwise unique.

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(9) If there are other species whose free energy changes during the reaction, for example, ions that intercalate (*e.g.*, in battery electrodes) or form ion pairs, these must be explicitly included in the electrochemical reaction (eq 9), and eq 10 must be modified appropriately.