Ch. 13: Electrochemistry

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Electrochemistry

Electrochemistry is a major branch of analytical chemistry that uses electrical measurements of chemical systems for analytical purposes, and also refers to the use of electricity to drive a chemical reaction or to the use of a chemical reaction to produce electricity.

High-capacity, rechargeable lithium-ion batteries, such as those in cell phones and laptop computers, are a shining example of the fruits of materials chemistry research.

- Li$^+$ intercalated in graphite layers migrate to cobalt oxide
- Electrons are left behind
- Porous polymer separator passes the Li$^+$ ions
- e- travel through circuit to CoO$_2$ to maintain neutrality

\[ \text{C}_6\text{Li} + \text{Li}_{1-x}\text{CoO}_2 \xrightarrow{\text{discharge}} \text{C}_6\text{Li}_{1-x} + \text{LiCoO}_2 \xleftarrow{\text{charge}} \]
Basic Concepts

A redox reaction involves transfer of electrons from one species to another.

- **Oxidation**: loss of electrons
- **Reduction**: gain of electrons
- **Oxidizing agent**: takes electrons
- **Reducing agent**: gives electrons

\[
\text{Fe}^{3+} + \text{V}^{2+} \rightarrow \text{Fe}^{2+} + \text{V}^{3+}
\]

When electrons from a redox reaction flow through an electric circuit, we can learn something about the reaction by measuring current and voltage.

- **Electric current** \((I)\) is proportional to the rate of reaction
- **Cell voltage** \((V)\) is proportional to the free energy change for the electrochemical reaction.

In techniques such as **voltammetry**, the voltage can be used to identify reactants.
Basic Concepts, 2

*Electric charge* \((q)\) is measured in *coulombs* \((C)\).
The magnitude of the charge of a single electron is \(1.602 \times 10^{-19} \text{ C}\), so a mole of electrons has a charge of \((1.602 \times 10^{-19} \text{ C})(6.022 \times 10^{23} \text{ mol}^{-1}) = 9.649 \times 10^4 \text{ C}\), which is called the Faraday constant, \(F\).

\[ q = n \cdot F \]

*Electric current* is the quantity of charge flowing each second through a circuit. The unit of current is the *ampere* \((A)\). A current of 1 A is a charge of 1 C s\(^{-1}\) flowing past a point in a circuit.

\[ 1 \text{ A} = 1 \text{ C s}^{-1} \]

The difference in *electric potential*, \(E\), between two points, is the work needed (or that can be done) when moving an electric charge from one point to the other. Potential difference is measured in *volts* \((V = J/C)\). The greater the potential difference, the stronger will be the "push" on a charged particle traveling between those points.

\[ w = E \cdot q \]

The *free energy change*, \(\Delta G\), for a chemical reaction conducted reversibly at constant temperature and pressure, equals the maximum possible electrical work that can be done by the reaction on its surroundings. The \(\Delta G\) is related to the electrical potential difference (i.e., the voltage).

\[ \Delta G = -w = -E \cdot q = -nFE \]
Basic Concepts, 3

Ohm’s law states that current, \( I \), is proportional to the potential difference (voltage) across a circuit and inversely proportional to the resistance, \( R \), of the circuit. Units of resistance are ohms (\( \Omega \)). A current of 1 A flows through a circuit with an \( E = 1 \) V if the \( R = 1 \) \( \Omega \).

\[
I = \frac{E}{R}
\]

Power, \( P \), is the work done per unit time. The SI unit of power is J/s, better known as the watt (W). Since \( P = \frac{w}{t} \), then \( P = Eq/t = E(q/t) = EI \). A cell capable of delivering 1 A at an \( E = 1 \) V has a power of \( P = 1 \) W.

\[
P = E \cdot I
\]

The power generated by the circuit appears as heat energy at the resistors (i.e., in absence of work for a 90 mW circuit, 90 mW of heat are generated at the resistors).

A circuit with a battery and a resistor. Benjamin Franklin investigated static electricity in the 1740s. He thought electricity was a fluid that flows from a silk cloth to a glass rod when the rod is rubbed with the cloth. We now know that electrons flow from glass to silk. However, Franklin’s convention for the direction of electric current has been retained, so we say that current flows from positive to negative—in the opposite direction of electron flow.
Charge and Quantity of Reaction

If 5.585 g of Fe$^{3+}$ is reduced, how many coulombs of charge must have been transferred from V$^{2+}$ to Fe$^{3+}$?

\[
\text{Fe}^{3+} + \text{V}^{2+} \rightarrow \text{Fe}^{2+} + \text{V}^{3+}
\]

**Oxidizing agent** **Reducing agent**

**Solution** First, we find that 5.585 g of Fe$^{3+}$ equal 0.100 0 mol of Fe$^{3+}$. Because each Fe$^{3+}$ ion requires one electron in **Reaction 13-1**, 0.100 0 mol of electrons must have been transferred. Using the Faraday constant, we find that 0.100 0 mol of electrons corresponds to

\[
q = nF = (0.100 \text{ mol } e^{-})(9.649 \times 10^4 \frac{\text{C}}{\text{mol } e^{-}}) = 9.649 \times 10^3 \text{ C}
\]

**Test Yourself** How many moles of Sn$^{4+}$ are reduced to Sn$^{2+}$ by 1.00 C of electric charge? *(Answer: 5.18 \mu\text{mol})*
Current and Rate of Reaction

Suppose that electrons are forced into a platinum wire immersed in a solution containing Sn⁴⁺, which is reduced to Sn²⁺ at a constant rate of 4.24 mmol/h. How much current passes through the solution?

**Solution**  Two electrons are required to reduce one Sn⁴⁺ ion:

\[ \text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+} \]

Electrons flow at a rate of \((2 \text{ mmol}^-/\text{mmol Sn}^{4+}) \times (4.24 \text{ mmol Sn}^{4+}/\text{h}) = 8.48 \text{ mmol e}^-/\text{h}\) which corresponds to

\[ \frac{8.48 \text{ mmol e}^-/\text{h}}{3600 \text{ s/h}} = 2.356 \times 10^{-3} \text{ mmol e}^-/\text{s} = 2.356 \times 10^{-6} \text{ mol e}^-/\text{s} \]

To find the current, we convert moles of electrons per second into coulombs per second:

\[
\text{Current} = \frac{\text{charge}}{\text{time}} = \frac{\text{coulombs}}{\text{second}} = \frac{\text{moles e}^-}{\text{second}} \cdot \frac{\text{coulombs}}{\text{mole}}
\]

\[
= \left(2.356 \times 10^{-6} \text{ mol} \right) \left(9.649 \times 10^4 \frac{\text{C}}{\text{mol}}\right)
\]

\[= 0.227 \text{ C/s} = 0.227 \text{ A} \]

**Test Yourself**  What current reduces Sn⁴⁺ at a rate of 1.00 mmol/h? (Answer: 53.6 mA)
Voltage and Electrical Work

How much work can be done if 2.4 mmol of electrons fall through a potential difference of 0.27 V?

Solution  To use Equation 13-3, we must convert moles of electrons into coulombs of charge. The relation is

\[ q = nF = (2.4 \times 10^{-3}\text{mol})(9.649 \times 10^4\text{C/mol}) = 2.3 \times 10^2\text{C} \]

The work that could be done is

\[ \text{work} = E \cdot q = (0.27\text{V})(2.3 \times 10^2\text{C}) = 62\text{J} \]

Test Yourself  What must be the potential drop (V) for 1.00 \( \mu \text{mol} \) e\(^-\) to do 1.00 J of work? (Answer: 10.4 V)

Analogies for current and voltage:

Electric current is analogous to volume of water per second flowing out of a hose.

Electric potential difference is analogous to the hydrostatic pressure pushing water through a hose. High pressure gives high flow.
Galvanic Cells

A *galvanic cell* (or *voltaic cell*) uses a spontaneous chemical reaction to generate electricity.

- one reagent must be oxidized and another must be reduced

- the two cannot be in contact, or electrons would flow directly from the reducing agent to the oxidizing agent.

- *batteries* (static compartments with reactants) and *fuel cells* (dynamic flow of reactants and products) consume their reactants to generate electricity.

Note: The Energizer bunny was recently arrested and charged with battery.
Galvanic Cells, 2

Consider the galvanic cell pictured below, featuring two electrodes suspended in a solution of CdCl$_2$. One electrode is Cd, and the other is metallic Ag coated with solid AgCl.

The net reaction is composed of a reduction and an oxidation, each of which is called a half-reaction.

The two half-reactions are written with equal numbers of electrons so that their sum includes no free electrons.

Oxidation of Cd metal to Cd$^{2+}$(aq) provides electrons that flow through the circuit to the Ag electrode. At the Ag surface, Ag$^+$ (from AgCl) is reduced to Ag(s), and Cl$^-$ goes into solution. The $\Delta G$ for the net reaction is $-150$ kJ per mole of Cd, provides the driving force that pushes electrons through the circuit (written example).
Consider the galvanic cell pictured below, featuring one Cd electrode and one Ag electrode. The solution contains Cd(NO₃)₂ and AgNO₃.

The net reaction is spontaneous, but little current flows through the circuit because Ag⁺ is not forced to be reduced at the Ag electrode.

Aqueous Ag⁺ can react directly at the Cd(s) surface, giving the same net reaction with no flow of electrons through the external circuit.

This cell is said to be short circuited.
Galvanic Cells, 4

To make a working cell, the reactants are separated into two half-cells which are connected with a salt bridge. The salt bridge is a U-shaped tube filled with a gel containing a high concentration of KNO$_3$ (or other electrolyte that does not affect the cell reaction). The ends of the bridge are porous glass disks that allow ions to diffuse but minimize mixing of solutions inside and outside the bridge.

K$^+$ from the bridge migrates into the cathode compartment and a small amount of NO$_3^-$ migrates from the cathode into the bridge. Ion migration offsets the charge buildup that would otherwise occur as electrons flow into the silver electrode.

At the left side of the salt bridge, NO$_3^-$ migrates into the anode compartment and a little Cd$^{2+}$ migrates into the bridge to prevent buildup of positive charge.

The migration of ions out of the bridge is greater than the migration of ions into the bridge because the salt concentration in the bridge is much higher than the salt concentration in the half-cells.

For reactions that do not involve Ag$^+$ or other species that react with Cl$^-$, the salt bridge usually contains KCl electrolyte. A typical salt bridge is prepared by heating 3 g of agar with 30 g of KCl in 100 mL of water until a clear solution is obtained. The solution is poured into the U-tube and allowed to gel. The bridge is stored in saturated aqueous KCl.
Galvanic Cells, 5

Electrochemical cells are described by *line notation*, which employs just two symbols:

\[ | \text{phase boundary} | \ || \text{salt bridge} | \]

The first cell we considered is denoted as:

\[ \text{Cd(s)} \ | \text{CdCl}_2(aq) \ | \text{AgCl(s)} \ | \text{Ag(s)} \]

The last cell we considered is denoted as:

\[ \text{Cd(s)} \ | \text{Cd(NO}_3)_2(aq) \ | \text{AgNO}_3(aq) \ | \text{Ag(s)} \]

Hence, the electrodes always are denoted on the outer sides, with single phase boundaries denoted by single vertical lines. The salt bridge symbol, \( \| \), represents the two phase boundaries on either side of the bridge.
Standard Potentials

In the electrochemical cells we have considered, the voltage, which is the difference in electrostatic potential between the two electrodes, also tells us how much work can be done by the electrons that are flowing from one side to the other.

The voltage is measured with a potentiometer (or voltmeter). Voltage is:
- **Positive**: electrons flow into the negative terminal (often coloured red)
- **Negative**: electrons flow into the positive terminal (often coloured black)

To predict the voltage that will be observed when different half-cells are connected, the *standard reduction potential*, $E^\circ$, for each half-cell is measured.

The term *standard* in this case means that activities of all species are equal to unity.
Standard Potentials, 2

The half reaction we are interested in is: \( \text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag} \ (\text{s}) \)
which occurs in the right half-cell (connected to positive terminal of potentiometer).

The left half-cell, connected to the negative terminal of the potentiometer, is called the standard hydrogen electrode (S.H.E.). It consists of a catalytic Pt surface in contact with an acidic solution in which the activity of the \( \text{H}^+ \) species is equal to unity. A stream of \( \text{H}_2(\text{g}) \) bubbled through the electrode saturates the solution with \( \text{H}_2(\text{aq}) \). The activity of \( \text{H}_2(\text{g}) \) is unity if the pressure of \( \text{H}_2(\text{g}) \) is 1 bar. The reaction that comes to equilibrium at the surface of the Pt electrode is called the S.H.E. half-reaction:

\[
\text{H}^+(aq, A = 1) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(g, A = 1)
\]

A potential value of zero if arbitrarily assigned to the S.H.E. at 25 °C, which allows us to assign the reading of voltage directly to the reaction occurring in the right half-cell (this acts as a reference potential, against which we can scale all other reduction potentials for reactions of interest). This value, \( E^\circ = +0.799 \text{ V} \), is the standard reduction potential for the reaction at the top, and the positive sign tells us that the electrons flow from left to right through the meter (i.e., to the negative terminal).

By convention, the left-hand electrode (Pt) is attached to the negative (reference) terminal of the potentiometer and the right-hand electrode is attached to the positive terminal.
Standard Potentials, 3

The half reaction we are interested in is: \[ \text{Cd}^{2+} + \text{e}^- \rightleftharpoons \text{Cd} \ (s) \]

we construct the cell: S.H.E. \( \text{||} \) \( \text{Cd}^{2+} \ (\text{aq}, A = 1) \ \text{||} \ \text{Cd}(s) \)

The Cd half-cell is connected to the positive terminal of the potentiometer. In this case, we observe \( E^0 = -0.402 \text{ V} \). The negative sign means that electrons flow from Cd to Pt, a direction opposite that of the cell in the case of the \( \text{Ag}^+ \) reduction.

**Challenge:** Sketch the set up for the reaction above, and show the direction of the flow of the current! (*written example*)
If some typical half-reactions are arranged according to descending value of $E^\circ$, we find the strongest oxidizing agents at the upper left and the strongest reducing agents at the lower right.

So: if two half cells featuring the $\text{Ag}^+$ and $\text{Cd}^{2+}$ reactions are connected, $\text{Ag}^+$ would be reduced to $\text{Ag(s)}$ as $\text{Cd(s)}$ is oxidized to $\text{Cd}^{2+}$.

The potential for the reduction of $\text{K}^+$ is $-2.936 \text{ V}$, meaning that $\text{K}^+$ is a very poor oxidizing agent. However, this does not automatically mean it is a great reducing agent, since it would have to easily give up electrons to form $\text{K}^{2+}$ (which it does not!). $\text{K(s)}$ on the other hand is a great reducing agent!
Le Châtelier’s principle tells us that increasing reactant concentrations drives a reaction to the right and increasing the product concentrations drives a reaction to the left. The net driving force for a reaction is expressed by the Nernst equation, whose two terms include the driving force under standard conditions ($E^\circ$, which applies when all activities are unity) and a term showing the dependence on reagent concentrations.

For the half reaction $aA + ne^- \rightleftharpoons bB$, the Nernst equation giving the half-cell potential, $E$, is

$$E = E^\circ - \frac{RT}{nF} \ln \frac{A^b_B}{A^a_A}$$

where $E^\circ = \text{standard reduction potential (activities} = 1)$, $n$ is the number of electrons involved in the half reaction, $F = 9.649 \times 10^4 \text{ C mol}^{-1}$, and $A_i$ are the activities of species $i$.

The logarithmic term involves a reaction quotient

$$Q = \frac{A^b_B}{A^a_A}$$

As usual, pure solids, pure liquids and solvents are assigned activity values of 1, and gases are expressed as pressures (in bar). If activities are all unity, $Q = 1$, $\ln Q = 0$, and $E = E^\circ$
Nernst Equation, 2

Converting the natural logarithm into the base 10 logarithm and inserting $T = 298.15 \text{ K}$ ($25.00 \ ^\circ\text{C}$) gives the most useful form of the Nernst equation:

$$E = E^\circ - \frac{0.05916 \ \text{V}}{n} \log \frac{A_B^b}{A_A^a}$$

which tells us that the potential changes by $59.16/n \ \text{mV}$ for each factor-of-10 change in $Q$.

EXAMPLE Writing the Nernst Equation for a Half-Reaction

Let's write the Nernst equation for the reduction of white phosphorus to phosphine gas:

$$\frac{1}{4} \text{P}_4(\text{s, white}) + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{PH}_3(\text{g}) \quad E^\circ = -0.046 \ \text{V}$$

Solution We omit solids from the reaction quotient, and the concentration of a gas is expressed as the pressure of the gas. Therefore, the Nernst equation is

$$E = E^\circ - \frac{0.05916}{3} \log \frac{P_{\text{PH}_3}}{[\text{H}^+]^3}$$

Test Yourself With $E^\circ$ from Appendix H, write the Nernst equation for $\text{ZnS(s)} + 2\text{e}^- = \text{Zn(s)} + \text{S}^2-$ (Answer: $E = -1.405 - \frac{0.05916}{2} \log [\text{S}^2-]$)
Nernst Equation, 3

Multiplying a half-reaction by any number does not change the standard reduction potential, $E^\circ$. The potential difference between two points is the work done per coulomb carried through that potential difference ($E = \text{work}/q$). Work per coulomb is the same whether 0.1, 2.3, or 104 coulombs have been transferred; however, the total work is different in each case. Therefore, we do not double $E^\circ$ if we multiply a half-reaction by 2.

Multiplying a half-reaction by any number does not change the half-cell potential, $E$. Consider a half-cell reaction written with either one or two electrons:

\[
\begin{align*}
\text{Ag}^+ + e^- &\rightleftharpoons \text{Ag(s)} \\
2\text{Ag}^+ + 2e^- &\rightleftharpoons 2\text{Ag(s)}
\end{align*}
\]

\[
E = E^\circ - 0.05916 \log \frac{1}{[\text{Ag}^+]} \quad \quad E = E^\circ - \frac{0.05916}{2} \log \frac{1}{[\text{Ag}^+]^2}
\]

The two expressions are equal because $\log a^b = b \log a$:

\[
\frac{0.05916}{2} \log \frac{1}{[\text{Ag}^+]^2} = \frac{2\gamma \times 0.05916}{2} \log \frac{1}{[\text{Ag}^+]}
\]

\[
= 0.05916 \log \frac{1}{[\text{Ag}^+]} \]

The exponent in the log term is canceled by the factor $1/n$ preceding the log term. Cell voltage is a measurable quantity that cannot depend on how you write the reaction.
Nernst Equation for a Complete Reaction

For a complete electrochemical cell, the Nernst equation expresses the measured voltage as the difference between the potentials of the two electrodes:

\[ E = E_+ + E_- \]

\( E_+ \): potential of the electrode attached to the positive terminal of the potentiometer
\( E_- \): potential of the electrode attached to the negative terminal.

The potential of each half-reaction (written as a reduction) is governed by a Nernst equation, and the voltage for the complete reaction is their difference.

If the net cell voltage, \( E = E_+ - E_- \), is positive, then the net cell reaction is spontaneous in the forward direction. If the net cell voltage is negative, then the reaction is spontaneous in the reverse direction.

That is:

\[ E > 0: \text{net cell reaction goes } \rightarrow \]

\[ E < 0: \text{net cell reaction goes } \leftarrow \]
To write a net cell reaction and find the associated voltage:

1. Write reduction half-reactions for both half-cells and find $E^\circ$ for each (Appendix H). Multiply the half-reactions as necessary so that they both contain the same number of electrons. N.B. When you multiply a reaction, you do not multiply $E^\circ$.

2. Write a Nernst equation for the right half-cell, which is attached to the positive terminal of the potentiometer. This is $E_+$. 

3. Write a Nernst equation for the left half-cell, which is attached to the negative terminal of the potentiometer. This is $E_-$.

4. Find the net cell voltage by subtraction: $E = E_+ - E_-$. 

5. Write the net cell reaction by subtracting the left half-reaction from the right half-reaction. (Subtraction is equivalent to reversing the left half-reaction and adding.)
**Nernst Equation for a Complete Reaction, 3**

*Example*: Find the voltage of the cell (with a salt bridge) if the right half-cell contains 0.50 M AgNO$_3$(aq) and the left half-cell contains 0.010 M Cd(NO$_3$)$_2$(aq). Write the net cell reaction and state whether it is spontaneous in the forward or reverse direction. (*written example*)

**Diagram:**

- **Anode**
  
  \[
  \text{Cd(s)} \rightarrow \text{Cd}^{2+}(aq) + 2e^- 
  \]

- **Cathode**
  
  \[
  2\text{Ag}^+(aq) + 2e^- \rightarrow 2\text{Ag(s)} 
  \]
Intuitive thoughts on cell potentials

$E$ for the Ag half-cell was 0.781 V and $E$ for the Cd half-cell was −0.461 V. Place these values on the number line and note that electrons always flow toward more positive potential. Therefore, electrons in the circuit flow from cadmium to silver. The separation of the two half-cells is 1.242 V. This diagram works the same way even if both half-cell potentials are positive or both are negative.
**$E^\circ$ and the Equilibrium Constant**

A galvanic cell produces electricity because the cell reaction is not at equilibrium. The potentiometer allows negligible current, so concentrations in the cell remain unchanged. If we replaced the potentiometer with a wire, there would be much more current and concentrations would change until the cell reached equilibrium. At that point, nothing would drive the reaction, and $E$ would be 0. When a galvanic cell runs down to 0 V, the chemicals inside have reached equilibrium, and the cell is "dead."

Relate $E$ for a whole cell to the reaction quotient, $Q$, for the net cell reaction.

Right electrode: 
\[ aA + ne^- \rightleftharpoons cC \quad E^+_e \]

Left electrode: 
\[ dD + ne^- \rightleftharpoons bB \quad E^-_e \]

Net cell reaction: 
\[ aA + bB \rightleftharpoons cC + dD \]

\[
E = E^+_e - E^-_e = E^\circ - \frac{0.059 \, 16}{n} \log \frac{[C]^c}{[A]^a} = \left( E^\circ - \frac{0.059 \, 16}{n} \log \frac{[B]^b}{[D]^d} \right)
\]

\[
E = (E^+_e - E^-_e) - \frac{0.059 \, 16}{n} \log \frac{[A]^c[D]^d}{[B]^a[C]^b} = E^\circ - \frac{0.059 \, 16}{n} \log Q
\]

This equation is true at any time. In the special case when the cell is at equilibrium, $E = 0$ and $Q = K$, the equilibrium constant.
$E^\circ$ and the Equilibrium Constant, 2

Therefore, at equilibrium, this equation becomes:

Finding $E^\circ$ from $K$:

$$E^\circ = \frac{0.059\ 16}{n} \log K$$

(at 25°C)

We can deduce $E^\circ$ from $K$, and vice versa.

Find the equilibrium constant for the reaction

$$\text{Cu(s)} + 2\text{Fe}^{3+} \rightleftharpoons 2\text{Fe}^{2+} + \text{Cu}^{2+}$$

**Solution** Divide the reaction into two half-reactions found in **Appendix H**:

$$2\text{Fe}^{3+} + 2e^- \rightleftharpoons 2\text{Fe}^{2+} \quad E^\circ_+ = 0.771 \text{ V}$$

$$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu(s)} \quad E^\circ_- = 0.339 \text{ V}$$

Then find $E^\circ$ for the net reaction

$$E^\circ = E^\circ_+ - E^\circ_- = 0.771 - 0.339 = 0.432 \text{ V}$$

and compute the equilibrium constant with **Equation 13-24**:

$$K = 10^{(2)(0.432)(\log 0.059\ 16)} = 4 \times 10^{14}$$

A modest value of $E^\circ$ produces a large equilibrium constant. The value of $K$ is correctly expressed with one significant figure, because $E^\circ$ has three digits. Two are used for the exponent (14), and one is left for the multiplier (4).
We can also find $K$ for net reactions that are not redox reactions. For example,

\[
\begin{align*}
- \text{FeCO}_3(s) + 2e^- & \rightleftharpoons \text{Fe}(s) + \text{CO}_3^{2-} \\
\text{Fe}^{2+} + 2e^- & \rightleftharpoons \text{Fe}(s) \\
\text{FeCO}_3(s) & \rightleftharpoons \text{Fe}^{2+} + \text{CO}_3^{2-}
\end{align*}
\]

From $E^\circ$ for the net reaction, we can compute $K_{sp}$ for iron(II) carbonate. Potentiometric measurements allow us to find equilibrium constants that are too small or too large to measure by determining concentrations of reactants and products directly. The reason for this is that the redox potential is just another way of expressing the change in Gibbs energy of the reaction: The more energetically favourable the reaction (the more negative $\Delta G^\circ$), the more positive is $E^\circ$. 

$E^\circ$ for dissolution of iron(II) carbonate is negative, which means that the reaction is "not spontaneous." "Not spontaneous" simply means $K < 1$. The reaction proceeds until the concentrations of reactants and products satisfy the equilibrium condition.
If you know $E^\circ_+$ and $E^\circ_-$, you can find $E^\circ$ and $K$ for the net cell reaction. Alternatively, if you know $E^\circ$ and either $E^\circ_+$ or $E^\circ_-$, you can find the missing standard potential. If you know $K$, you can calculate $E^\circ$ and use it to find either $E^\circ_+$ or $E^\circ_-$, provided you know one of them.
$E^\circ$ and the Equilibrium Constant, 5

Relating $E^\circ$ and $K$:

From the formation constant of Ni(glycine)$_2$ plus $E^\circ$ for the Ni$^{2+}$ | Ni(s) couple,

\[
\begin{align*}
\text{Ni}^{2+} + 2 \text{glycine}^- & \rightleftharpoons \text{Ni(glycine)}_2 & K = \beta_2 = 1.2 \times 10^{11} \\
\text{Ni}^{2+} + 2e^- & \rightleftharpoons \text{Ni(s)} & E^\circ = -0.236 \text{ V}
\end{align*}
\]

deduce the value of $E^\circ$ for the reaction

\[
\begin{align*}
\text{Ni(glycine)}_2 + 2e^- & \rightleftharpoons \text{Ni(s)} + 2 \text{glycine}^- & (13-25)
\end{align*}
\]

**Solution** We need to see the relations among the three reactions:

\[
\begin{align*}
\text{Ni}^{2+} + 2e^- & \rightleftharpoons \text{Ni(s)} & E^\circ_+ = -0.236 \text{ V} \\
\text{Ni(glycine)}_2 + 2e^- & \rightleftharpoons \text{Ni(s)} + 2 \text{glycine}^- & E^\circ_- = ? \\
\text{Ni}^{2+} + 2 \text{glycine}^- & \rightleftharpoons \text{Ni(glycine)}_2 & E^\circ = ? & K = 1.2 \times 10^{11}
\end{align*}
\]

We know that $E^\circ_+ - E^\circ_-$ must equal $E^\circ$, so we can deduce the value of $E^\circ_-$ if we can find $E^\circ$. But $E^\circ$ can be determined from the equilibrium constant for the net reaction:

\[
E^\circ = \frac{0.05916}{n} \log K = \frac{0.05916}{2} \log(1.2 \times 10^{11}) = 0.328 \text{ V}
\]

Hence, the standard reduction potential for half-reaction 13-25 is

\[
E^- = E^\circ_+ - E^\circ = -0.236 - 0.328 = -0.564 \text{ V}
\]
Cells as Chemical Probes

We must distinguish two classes of equilibria associated with galvanic cells:

1. Equilibrium between the two half-cells
2. Equilibrium within each half-cell

If a galvanic cell has a nonzero voltage, then the net cell reaction is not at equilibrium. We say that equilibrium between the two half-cells has not been established. We allow half-cells to stand long enough to come to chemical equilibrium within each half-cell.

Consider the following cell. It can be set up to measure the pH in the left hand container!

This is at equilibrium:

\[ \text{AgCl(s)} \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \]

as is this:

\[ \text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2\text{H}^- + \text{H}^+ \]

Neither is part of the net cell redox reaction.
The redox reaction for the right half-cell is

\[
\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-(aq, 0.10 \text{ M}) \quad E^\circ_+ = 0.222 \text{ V}
\]

For the left-hand cell, we see that \( \text{H}_2(\text{g}) \) bubbles into the cell, and that every aqueous solution contains \( \text{H}^+ \). Therefore, hydrogen is present in two oxidation states, and the half-reaction can be written as

\[
2\text{H}^+(aq, ? \text{ M}) + 2e^- \rightleftharpoons \text{H}_2(\text{g}, 1.00 \text{ bar}) \quad E^\circ_- = 0
\]

The net cell reaction is not at equilibrium, because the measured voltage is 0.503 V (as shown in the figure on the previous slide), not 0 V. The Nernst equation for the net cell is:

\[
E = E^\circ_+ - E^- = (0.222 - 0.05916 \log[\text{Cl}^-]) - \left(0 - \frac{0.05916}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2}\right)
\]

Solve for the only unknown, which happens to be \([\text{H}^+]\), and then evaluate \( pK_a \):

\[
0.503 = (0.222 - 0.05916 \log[0.10]) - \left(0 - \frac{0.05916}{2} \log \frac{1.00}{[\text{H}^+]^2}\right)
\]

\[
\Rightarrow [\text{H}^+] = 1.8 \times 10^{-4} \text{ M}
\]

\[
K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(0.0050)(1.8 \times 10^{-4})}{0.050} = 1.8 \times 10^{-5}
\]
Tips for Analyzing Cells

In many cases, you must find an equilibrium constant for a reaction that occurs in only one half-cell. The reaction of interest is not the net cell reaction and is not a redox reaction. Proceed as follows:

1. Write the two half-reactions and their standard potentials. If you choose a half-reaction for which you cannot find $E^\circ$, then find another way to write the reaction.

2. Write a Nernst equation for the net reaction and put in all the known quantities. If all is well, there will be only one unknown in the equation.

3. Solve for the unknown concentration and use that concentration to solve the chemical equilibrium problem that was originally posed.
Biochemists use $E_0'$

If $H^+$ is involved in the reaction, $E^o$ applies when $pH = 0$ ($[H^+] = 1$). Whenever $H^+$ appears in a redox reaction, or whenever reactants or products are acids or bases, reduction potentials are pH dependent.

Because the pH inside a plant or animal cell is about 7, reduction potentials that apply at pH 0 are not particularly appropriate (or relevant to living cells, in which many interesting standard reduction potentials can be calculated).

The formal potential is the reduction potential that applies under a specified set of conditions (including pH, ionic strength, and concentration of complexing agents). Biochemists call the formal potential at pH 7 $E_0'$ (read "$E$ zero prime").

For the half reaction: $aA + ne^- \rightleftharpoons bB + mH^+$ ($E^o$), the Nernst equation is

$$E = E^o - \frac{0.05916}{n} \log \frac{[B]^b[H^+]^m}{[A]^a}$$

To find $E_0'$, rearrange to a form containing the formal concentrations of A and B (powers of $a$ and $b$); the entire collection of terms over the brace is called $E_0'$:

$$Recipe ~for ~E_0' : ~E = E^o + other ~terms ~- \frac{0.05916}{n} \log \frac{F_B^b}{F_A^a}$$

All of this is called $E_0'$ when pH = 7
Biochemists use $E^\circ$, 2

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^\circ$ (V)</th>
<th>$E^\circ'$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$</td>
<td>+1.229</td>
<td>+0.815</td>
</tr>
<tr>
<td>$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$</td>
<td>+0.771</td>
<td>+0.771</td>
</tr>
<tr>
<td>$I_2 + 2e^- = 2I^-$</td>
<td>+0.535</td>
<td>+0.535</td>
</tr>
<tr>
<td>Cytochrome $a$ ($Fe^{3+}$) $+$ $e^-$ $\rightleftharpoons$ cytochrome $a$ ($Fe^{2+}$)</td>
<td>+0.290</td>
<td>+0.290</td>
</tr>
<tr>
<td>$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$</td>
<td>+0.695</td>
<td>+0.281</td>
</tr>
<tr>
<td>Cytochrome $c$ ($Fe^{3+}$) $+$ $e^-$ $\rightleftharpoons$ cytochrome $c$ ($Fe^{2+}$)</td>
<td>-</td>
<td>+0.254</td>
</tr>
<tr>
<td>2,6-Dichlorophenolindophenol $+$ $2H^+ + 2e^- \rightleftharpoons$ reduced 2,6-dichlorophenolindophenol</td>
<td>-</td>
<td>+0.22</td>
</tr>
<tr>
<td>Dehyroascorbate $+$ $2H^+ + 2e^- \rightleftharpoons$ ascorbate $+$ $H_2O$</td>
<td>+0.390</td>
<td>+0.058</td>
</tr>
<tr>
<td>Fumarate $+$ $2H^+ + 2e^- \rightleftharpoons$ succinate</td>
<td>+0.433</td>
<td>+0.031</td>
</tr>
<tr>
<td>Methylene blue $+$ $2H^+ + 2e^- \rightleftharpoons$ reduced product</td>
<td>+0.532</td>
<td>+0.011</td>
</tr>
<tr>
<td>Glyoxylate $+$ $2H^+ + 2e^- \rightleftharpoons$ glycolate</td>
<td>-</td>
<td>-0.090</td>
</tr>
<tr>
<td>Oxaloacetate $+$ $2H^+ + 2e^- \rightleftharpoons$ malate</td>
<td>+0.330</td>
<td>-0.102</td>
</tr>
<tr>
<td>Pyruvate $+$ $2H^+ + 2e^- \rightleftharpoons$ lactate</td>
<td>+0.224</td>
<td>-0.190</td>
</tr>
<tr>
<td>Riboflavin $+$ $2H^+ + 2e^- \rightleftharpoons$ reduced riboflavin</td>
<td>-</td>
<td>-0.208</td>
</tr>
<tr>
<td>FAD $+$ $2H^+ + 2e^- \rightleftharpoons$ FADH$_2$</td>
<td>-</td>
<td>-0.219</td>
</tr>
<tr>
<td>(Glutathione-S)$_2$ $+$ $2H^+ + 2e^- \rightleftharpoons$ 2 glutathione-SH</td>
<td>-</td>
<td>-0.23</td>
</tr>
<tr>
<td>Safranine T $+$ $2e^- \rightleftharpoons$ leucosafranine T</td>
<td>-0.235</td>
<td>-0.289</td>
</tr>
<tr>
<td>($C_6H_7S$)$_2$ $+$ $2H^+ + 2e^- \rightleftharpoons$ $2C_6H_5SH$</td>
<td>-</td>
<td>-0.30</td>
</tr>
<tr>
<td>NAD$^+$ $+$ $H^+ + 2e^- \rightleftharpoons$ NADH</td>
<td>-0.105</td>
<td>-0.320</td>
</tr>
<tr>
<td>NADP$^+$ $+$ $H^+ + 2e^- \rightleftharpoons$ NADPH</td>
<td>-</td>
<td>-0.324</td>
</tr>
<tr>
<td>Cystine $+$ $2H^+ + 2e^- \rightleftharpoons$ 2 cysteine</td>
<td>-</td>
<td>-0.340</td>
</tr>
<tr>
<td>Acetoacetate $+$ $2H^+ + 2e^- \rightleftharpoons$ L-β-hydroxybutyrate</td>
<td>-</td>
<td>-0.346</td>
</tr>
<tr>
<td>Xanthine $+$ $2H^+ + 2e^- \rightleftharpoons$ hypoxanthine $+$ $H_2O$</td>
<td>-</td>
<td>-0.371</td>
</tr>
<tr>
<td>$2H^+ + 2e^- \rightleftharpoons$ $H_2$</td>
<td>0.000</td>
<td>-0.414</td>
</tr>
<tr>
<td>Gluconate $+$ $2H^+ + 2e^- \rightleftharpoons$ glucose $+$ $H_2O$</td>
<td>-</td>
<td>-0.44</td>
</tr>
<tr>
<td>$SO_4^{2-} + 2e^- + 2H^+ \rightleftharpoons SO_3^{2-} + H_2O$</td>
<td>-</td>
<td>-0.454</td>
</tr>
<tr>
<td>$2SO_4^{2-} + 2e^- + 4H^+ \rightleftharpoons S_2O_4^{2-} + 2H_2O$</td>
<td>-</td>
<td>-0.527</td>
</tr>
</tbody>
</table>