Electrochemical Properties of Materials for Electrical Energy Storage Applications

Lecture Note 2

September 4, 2013

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<tr>
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Electrochemical Cell

The opposite charges built up on the electrodes produce an emf that causes current to flow.
Li Secondary Batteries

Electrode 1 / Electrolytic Solution / Electrode 2

interface 1

interface 2
Electrode 1 / Electrolytic Solution / Electrode 2

Interface 1                      Interface 2

A single interface at Electrode / Electrolytic Solution
- Interface: a site for an electrochemical reaction of interest
- Electrochemical reaction: heterogeneous reaction

Factors affecting electrode reaction rate and current
1. Mass transfer
2. Electron transfer at the electrode surface
3. Chemical reactions
4. Other surface reactions: adsorption, desorption, electrodeposition

Figure 1.3.6 Pathway of a general electrode reaction.
Electrochemical Cell

- The metals in a cell are called the **electrodes (electronic conductors)**, and the chemical solution is called the **electrolyte (ionic conductor)**.

- The electrolyte **reacts oppositely** with the two different electrodes.

- It causes **one electrode to lose electrons and develop a +ve charge (oxidation)**; and the other electrode to build a surplus of electrons and develop a –charge (reduction).

- The difference in potential between the two electrode charges is **the cell voltage**.
Electrochemical Cell

The opposite charges built up on the electrodes produce an emf that causes current to flow.

Electrode/electrolytic solution interface
Materials Electrochemistry

Electrode / Electrolytic Solution

- Electrode: electronic conductor (Electrode Materials)
- Electrolytic solution: ionic conductor (Ionics)
- Interface at Electrode / Electrolytic Solution: (Electrodics)

☞ interface between electronic conductor and ionic conductor

Electrochemical reaction: charge transfer reaction

\[ \text{Li}^+ \text{ (solution)} + e^- \text{ (electrode)} \rightarrow \text{Li} \text{ (electrode)} \]

Chemical reaction:

- mass balance
- charge balance (electrochemical reaction)
- site balance (solid state reaction)
Electrochemical Cell

What does the Black Box do to turn on the light bulb?
Battery: provides continuous supply of electrons to light a bulb

Battery: Electron Pump

- Current flow direction?
  from +ve terminal to -ve terminal through an external circuit

- Electron flow direction?
  opposite to a current flow direction

Current: amount of electric charge per unit time
(i = dq/dt)
Batteries

Current flow and potential difference:
Head and tail of a coin

Current flow exists only when there is a potential difference between two points in an electronic conductor.

There is a potential difference between two points in an electronic conductor whenever there is a current.

Fig. - A simple circuit in which a battery provides power for a light bulb.
Batteries

What happens when a battery operates?

- How is a potential difference between +ve and –ve terminals developed?

- Which reaction gives its unique potential value to a terminal (or electrode)?

- What makes it possible to pump electrons from –ve electrode to +ve electrode?

- Which reaction produces electrons?

- Which reaction consumes electrons?

- What is a electrical work for such an electron transport from –ve electrode to +ve electrode?
Oxidation State

Vanadium forms a number of different ions - for example, $V^{2+}$ and $V^{3+}$.

The $2^+$ ion will be formed by oxidising the metal by removing two electrons:

$$ V \quad \rightarrow \quad V^{2+} + 2e^- $$

The vanadium is now said to be in an oxidation state of $+2$.

Removal of another electron gives the $V^{3+}$ ion:

$$ V^{2+} \quad \rightarrow \quad V^{3+} + e^- $$

The vanadium now has an oxidation state of $+3$.

Removal of another electron gives a more unusual looking ion, $VO^{2+}$.

$$ V^{3+} + H_2O \quad \rightarrow \quad VO^{2+} + 2H^+ + e^- $$

The vanadium is now in an oxidation state of $+4$. Notice that the oxidation state isn't simply counting the charge on the ion (that was true for the first two cases but not for this one).

The positive oxidation state is counting the total number of electrons which have had to be removed - starting from the element.
Oxidation and Reduction

**Oxidation and reduction in terms of electron transfer**
Oxidation is loss of electrons.
Reduction is gain of electrons.

CuO + Mg → Cu + MgO

The magnesium is reducing the copper(II) ions by giving them electrons to neutralise the charge.
Magnesium is a reducing agent.

Looking at it the other way round, the copper(II) ions are removing electrons from the magnesium to create the magnesium ions.
The copper(II) ions are acting as an oxidising agent.
Reaction at each electrode (half cell reaction)

Differing reactivities of metals of Mg and Cu:

When metals react, they give away electrons and form positive ions. This particular topic sets about comparing the ease with which a metal does this to form hydrated ions in solution - for example, $\text{Mg}^{2+}(\text{aq})$ or $\text{Cu}^{2+}(\text{aq})$.

Half cell reaction written as a reduction reaction

\[
\begin{align*}
\text{Mg}(s) & \rightarrow \text{Mg}^{2+}(\text{aq}) + 2e^- \\
\text{Cu}(s) & \rightarrow \text{Cu}^{2+}(\text{aq}) + 2e^- 
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- A substance which picks up electrons from something else is an oxidising agent.
- The more positive the $E^\circ$ value, the stronger the substances on the left-hand side of the equation are as oxidising agents.
- Chlorine gas is the strongest oxidising agent ($E^\circ = +1.36$ v).
- A solution containing dichromate(VI) ions in acid is almost as strong an oxidising agent ($E^\circ = +1.33$ v).
- None of these three are as strong an oxidising agent as Au$^{3+}$ ions ($E^\circ = +1.50$ v).
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Isolated containers of Zn in ZnSO$_4$ and Cu in CuSO$_4$

How do you describe equilibrium?

When the two containers are isolated from one another, their contents don’t appear to change. Their electrodes neither grow nor shrink and the solutions remain the same. But this constancy doesn’t mean that nothing is happening in the containers. In fact, zinc and copper ions are constantly departing and arriving at the surfaces of the electrodes.

Zinc and copper ions are soluble because they polarize the water molecules, which then carry them around in solution. In contrast, zinc and copper atoms don’t polarize the water molecules and are insoluble. Thus for an atom to leave an electrode, it must give up two electrons to the electrode and enter the water as an ion. Similarly, for an ion to return to an electrode, it must pick up two electrons from the electrode and leave the water as an atom.

In an isolated container, this exchange quickly reaches a chemical equilibrium, with equal numbers of ions leaving and returning to the electrode each second. If too many ions leave the electrode, the solution becomes positively charged and pushes ions back toward the electrode. If too few ions leave the electrode, the solution becomes negatively charged and pulls ions off the electrode. These balancing effects stabilize the chemical equilibrium. The containers remain electrically neutral.
In the magnesium case, there is a lot of difference between the negativeness of the metal and the positiveness of the solution around it. In the copper case, the difference is much less.

This potential difference could be recorded as a voltage - the bigger the difference between the positiveness and the negativeness, the bigger the voltage. Unfortunately, that voltage is impossible to measure!

It would be easy to connect a voltmeter to the piece of metal, but how would you make a connection to the solution? By putting a probe into the solution near the metal? No - it wouldn't work!
Reaction at each electrode (half cell reaction)

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

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

Voltmeter
Reaction at each electrode (half cell reaction)

\[ \text{Mg}^{2+}_{(aq)} + 2e^- \rightarrow \text{Mg}_{(s)} \]

\[ \text{Cu}^{2+}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)} \]

Any probe you put in is going to have a similar sort of equilibrium happening around it. The best you could measure would be some sort of combination of the effects at the probe and the piece of metal you are testing.
Reaction at each electrode (half cell reaction)

Suppose you had an optical device for measuring heights some distance away, and wanted to use it to find out how tall a particular person was. Unfortunately, you can't see their feet because they are standing in long grass.

Although you can't measure their absolute height, what you can do is to measure their height relative to the convenient post. Suppose that in this case, the person turned out to be 15 cm taller than the post.
You could repeat this for a range of people . . .

Although you don't know any of their absolute heights, you can usefully rank them in order, and do some very simple sums to work out exactly how much taller one is than another.

<table>
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Reaction at each electrode (half cell reaction)

This turns out to be exactly what we need to do with the equilibria we started talking about. We don't actually need to know the absolute position of any of these equilibria. Going back to the magnesium and copper equilibria:

All we need to know is that the magnesium equilibrium lies further to the left than the copper one. (equilibrium constant)

\[
\text{Mg}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Mg}_{(s)} \quad \text{Cu}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Cu}_{(s)}
\]

We need to know that magnesium sheds electrons and forms ions more readily than copper does. That means that we don't need to be able to measure the absolute voltage between the metal and the solution.

It is enough to compare the voltage measured with a standardised system called a reference electrode. The system used is called a standard hydrogen electrode.
Reaction at each electrode (half cell reaction)

**Standard hydrogen electrode**

As the hydrogen gas flows over the porous platinum, an equilibrium is set up between hydrogen molecules and hydrogen ions in solution. The reaction is catalysed by the platinum.

\[ 2H^+_{(aq)} + 2e^- \rightleftharpoons H_2(g) \]

This is the equilibrium that we are going to compare all the others with.

**Standard conditions:**
- Hydrogen pressure is 1 bar (100 kPa). (You may find 1 atmosphere quoted in older sources.)
- Temperature is 298 K (25°C).
- All ions concentrations are taken as being 1 mol dm\(^{-3}\).
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Reaction at each electrode (half cell reaction)

There is a major difference between the charge on the two electrodes - a potential difference which can be measured with a voltmeter. The voltage measured would be 2.37 volts and the voltmeter would show the magnesium as the negative electrode and the hydrogen electrode as being positive.

The copper is the more positive (less negative) electrode. The voltage measured would be 0.34 volts. The voltmeter will show the hydrogen electrode as the negative one and the copper electrode as positive.
Reaction at each electrode (half cell reaction)

You may have noticed that the voltmeter was described as having a "high input resistance". Ideally, it wants to have an infinitely high input resistance.

This is to avoid any flow of current through the circuit. If there was a low resistance in the circuit, electrons would flow from where there are a lot of them (around the magnesium, for example) to where there are less (on the hydrogen electrode).

If any current flows, the voltage measured drops. In order to make proper comparisons, it is important to measure the maximum possible voltage in any situation. This is called the *electromotive force* or *emf*.

The emf of a cell measured under standard conditions is given the symbol $E^{\circ}_{\text{cell}}$.

You read $E^{\circ}$ as "E nought" or "E standard".
Reaction at each electrode (half cell reaction)

Cell conventions

Pt | H₂(g) | 2H⁺(aq) || or Pt [H₂(g)] | H⁺(aq) ||

Square brackets replaced by a vertical line showing the boundary between the platinum and the hydrogen.

One hydrogen ion shown rather than the 2 from the equation.
Reaction at each electrode (half cell reaction)

**Cell conventions**

- Square brackets show the hydrogen flowing over the platinum.
- Single vertical lines show a boundary between two phases - for example, between the magnesium ions and the solid metal.
- Double vertical lines show the salt bridge. This is sometimes shown by a single (or double) broken vertical line (or lines).
Reaction at each electrode (half cell reaction)

\[
\begin{align*}
\text{Pt} & | \text{H}_2(g) | 2\text{H}^+(aq) \ || \ Mg^{2+}(aq) | Mg(s) \quad E_{\text{cell}}^0 = -2.37 \text{ V} \\
& \quad \quad \quad \quad \text{Shows that the magnesium (the right-hand electrode) is the negative one.}
\end{align*}
\]

\[
\begin{align*}
\text{Pt} & | \text{H}_2(g) | 2\text{H}^+(aq) \ || \ Cu^{2+}(aq) | Cu(s) \quad E_{\text{cell}}^0 = +0.34 \text{ V} \\
& \quad \quad \quad \quad \text{Shows that the copper (the right-hand electrode) is the positive one.}
\end{align*}
\]

Remember that the standard electrode potential of a metal / metal ion combination is the emf measured when that metal / metal ion electrode is coupled to a hydrogen electrode under standard conditions.
Oxidation and Reduction

Measuring redox potentials for systems involving gases

The obvious example here is chlorine. Chlorine is well known as an oxidising agent. This time we are measuring the position of this equilibrium relative to the hydrogen equilibrium.

\[
\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-_{(\text{aq})}
\]

How can this equilibrium be connected into a circuit? The half-cell is built just the same as a hydrogen electrode. Chlorine gas is bubbled over a platinum electrode, which is immersed in a solution containing chloride ions with a concentration of 1 mol dm\(^{-3}\).

The conventional way of writing the whole cell looks like this.

\[
\text{Pt(s)} \ [\text{H}_2(\text{g})] \ | \ 2\text{H}^+_{(\text{aq})} \ || \ \text{Cl}_2(\text{g}) \ | \ 2\text{Cl}^-_{(\text{aq})} \ | \ \text{Pt(s)}
\]

\[E^0 = +1.36 \text{ V}\]

That means that the position of the \(\text{Cl}_2 / \text{Cl}^-\) equilibrium lies more to the right than the hydrogen equilibrium. Chlorine is much more likely to pick up electrons than hydrogen ions are.
Oxidation and Reduction

*The Fe$^{2+} / Fe^{3+}$ system*

Iron(II) ions are easily oxidised to iron(III) ions, and iron(III) ions are fairly easily reduced to iron(II) ions.

\[
Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)
\]

To measure the redox potential of this, you would simply insert a platinum electrode into a beaker containing a solution containing both iron(II) and iron(III) ions (1 mol dm$^{-3}$ with respect to both), and couple this to a hydrogen electrode.

The cell diagram would look like this:

\[
Pt(s) \ [H_2(g)] \ || \ 2H^+(aq) \ || \ Fe^{3+}(aq), Fe^{2+}(aq) \ || \ Pt(s)
\]

\[E^0 = +0.77 \text{ V}\]

Notice that the $E^0$ value isn't as positive as the chlorine one. The position of the iron(III) / iron(II) equilibrium isn't as far to the right as the chlorine equilibrium. That means that Fe$^{3+}$ ions don't pick up electrons as easily as chlorine does. Chlorine is a stronger oxidising agent than Fe$^{3+}$ ions.
Potassium dichromate(VI) as an oxidising agent

A commonly used oxidising agent, especially in organic chemistry, is potassium dichromate(VI) solution acidified with dilute sulphuric acid. The potassium ions are just spectator ions and aren't involved in the equilibrium in any way.

\[
\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)
\]

The half cell would have a piece of platinum dipping into a solution containing all the ions (dichromate(VI) ions, hydrogen ions and chromium(III) ions) all at 1 mol dm\(^{-3}\).

\[
\text{hydrogen electrode} \quad \|$ \quad [\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq)] , [2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)] \quad | \quad \text{Pt(s)}
\]

\[
E^0 = +1.33 \text{ V}
\]
Nernst Equation

\[ O + ne = R \]

\[ E = E^o - \left( \frac{RT}{nF} \right) \left( \frac{a_R}{a_O} \right), \quad E^o = ? \]

\[ E = E^{o'} - \left( \frac{RT}{nF} \right) \left( \frac{C_R}{C_O} \right), \quad E^{o'} = \text{formal potential} \]

If the system follows the Nernst equation, the electrode reaction is often said to be thermodynamically or electrochemically reversible (or nernstian).

Reversibility of a process; one’s ability to detect the signs of disequilibrium

Rate of change of force driving the observed process vs. speed with which the system can reestablish equilibrium

If the perturbation applied to the system is small enough, or if the system can attain equilibrium rapidly enough compared to the measuring time, thermodynamic relation will apply.
Electrochemical series

Equilibrium potential measured vs. SHE (Standard Hydrogen Electrode)

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>$E^\circ$ (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}^+\text{(aq)} + e^- \rightleftharpoons \text{Li(s)}$</td>
<td>-3.03</td>
</tr>
<tr>
<td>$\text{K}^+\text{(aq)} + e^- \rightleftharpoons \text{K(s)}$</td>
<td>-2.92</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Ca(s)}$</td>
<td>-2.87</td>
</tr>
<tr>
<td>$\text{Na}^+\text{(aq)} + e^- \rightleftharpoons \text{Na(s)}$</td>
<td>-2.71</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Mg(s)}$</td>
<td>-2.37</td>
</tr>
<tr>
<td>$\text{Al}^{3+}\text{(aq)} + 3e^- \rightleftharpoons \text{Al(s)}$</td>
<td>-1.66</td>
</tr>
<tr>
<td>$\text{Zn}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Zn(s)}$</td>
<td>-0.76</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Fe(s)}$</td>
<td>-0.44</td>
</tr>
<tr>
<td>$\text{Pb}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Pb(s)}$</td>
<td>-0.13</td>
</tr>
<tr>
<td>$2\text{H}^+\text{(aq)} + 2e^- \rightleftharpoons \text{H}_2\text{(g)}$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Cu(s)}$</td>
<td>+0.34</td>
</tr>
<tr>
<td>$\text{Ag}^+\text{(aq)} + e^- \rightleftharpoons \text{Ag(s)}$</td>
<td>+0.80</td>
</tr>
<tr>
<td>$\text{Au}^{3+}\text{(aq)} + 3e^- \rightleftharpoons \text{Au(s)}$</td>
<td>+1.50</td>
</tr>
</tbody>
</table>

The more negative the $E^\circ$ value, the more the position of equilibrium lies to the left - the more readily the metal loses electrons. The more negative the value, the stronger reducing agent the metal is.

The more positive the $E^\circ$ value, the more the position of equilibrium lies to the right - the less readily the metal loses electrons, and the more readily its ions pick them up again. The more positive the value, the stronger oxidising agent the metal ion is.
**REDOX POTENTIALS**

**Combining a zinc with a copper half cell**

So far, we have looked at combinations of a hydrogen electrode with the half cell we have been interested in. What happens if you combine a zinc half cell with a copper half cell?

**In the presence of a high resistance voltmeter**

The two equilibria which are set up in the half cells are:

\[
\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn} (s) \quad \text{E}^\circ = -0.76 \text{ v}
\]

\[
\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu} (s) \quad \text{E}^\circ = +0.34 \text{ v}
\]

The negative sign of the zinc E° value shows that it releases electrons more readily than hydrogen does. The positive sign of the copper E° shows that it releases electrons less readily than hydrogen.

That means that you can compare any two equilibria directly. For example, in this case you can see that the zinc releases electrons more readily than the copper does - the position of the zinc equilibrium lies further to the left than the copper equilibrium.
REDOX POTENTIALS

Stripping everything else out of the diagram, and looking only at the build up of electrons on the two pieces of metal:

Removing the voltmeter

The high resistance of the voltmeter is deliberately designed to stop any current flow in the circuit. What happens if you remove the voltmeter and replace it with a bit of wire?

Electrons will flow from where there are a lot of them (on the zinc) to where there are fewer (on the copper). The movement of the electrons is an electrical current.
Electrons are flowing away from the zinc equilibrium. According to Le Chatelier's Principle, the position of equilibrium will move to replace the lost electrons.

Electrons are being dumped onto the piece of copper in the copper equilibrium. According to Le Chatelier's Principle, the position of equilibrium will move to remove these extra electrons.

If electrons continue to flow, the positions of equilibrium keep on shifting. The two equilibria essentially turn into two one-way reactions. The zinc continues to ionise, and the copper(II) ions keep on picking up electrons.

\[
\begin{align*}
\text{Zn}^{2+}(aq) + 2e^- & \rightleftharpoons \text{Zn}(s) & E^0 = -0.76 \text{ V} \\
\text{Cu}^{2+}(aq) + 2e^- & \rightleftharpoons \text{Cu}(s) & E^0 = +0.34 \text{ V}
\end{align*}
\]
**REDOX POTENTIALS**

**What occurs when you drop a piece of zinc into some copper(II) sulphate solution?**

The blue color of the copper sulphate solution fades as the copper(II) ions are converted into brown copper metal. The final solution contains zinc sulphate. (The sulphate ions are spectator ions.)

You can add the two electron-half-equations above to give the overall ionic equation for the reaction:

\[ \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \]
\[ \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \]

\[ \text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s) \]

The only difference in this case is that the zinc gives the electrons *directly* to the copper(II) ions rather than the electrons having to travel along an external circuit.
Reaction at each electrode (half cell reaction)

What you are doing is comparing the position of the metal/metal ion equilibrium with the equilibrium involving hydrogen.

<table>
<thead>
<tr>
<th>metal / metal ion combination</th>
<th>$E^\circ$ (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$/Mg</td>
<td>-2.37</td>
</tr>
<tr>
<td>Zn$^{2+}$/Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Cu$^{2+}$/Cu</td>
<td>+0.34</td>
</tr>
<tr>
<td>Ag$^+$/Ag</td>
<td>+0.80</td>
</tr>
</tbody>
</table>

If you compare these with the $E^\circ$ values, you can see that the ones whose positions of equilibrium lie furthest to the left have the most negative $E^\circ$ values. That is because they form ions more readily - and leave more electrons behind on the metal, making it more negative.
Those which don't shed electrons as readily have positions of equilibrium further to the right. Their $E^\circ$ values get progressively more positive.
**REDOX POTENTIALS**

E° values are positive. Neither copper nor silver produce ions and release electrons as easily as hydrogen does.

However, of the two, copper releases electrons more readily. In a cell, the copper would have the greater build up of electrons, and be the negative electrode. If the copper and silver were connected by a bit of wire, electrons would flow from the copper to the silver.

Whenever you link two of these equilibria together: The equilibrium with the more negative (or less positive) E° value will move to the left. The equilibrium with the more positive (or less negative) E° value will move to the right.
Magnesium reacts with dilute sulphuric acid to give hydrogen and a colourless solution containing magnesium sulphate.

Is this what you would expect from the $E^\circ$ values?
Potassium dichromate(VI) acidified with dilute sulphuric acid oxidises iron(II) ions to iron(III) ions. The orange solution containing the dichromate(VI) ions turns green as chromium(III) ions are formed.

Electrons are flowing from the Fe$^{3+}$/Fe$^{2+}$ equilibrium to potassium dichromate equilibrium.
**REDOX POTENTIALS**

**Predicting the feasibility of a possible redox reaction**

Standard electrode potentials (redox potentials) are one way of measuring how easily a substance loses electrons. In particular, they give a measure of relative positions of equilibrium in reactions such as:

\[
\begin{align*}
\text{Zn}^{2+}_{(aq)} + 2e^- & \rightleftharpoons \text{Zn}_{(s)} \quad E^o = -0.76 \text{ v} \\
\text{Cu}^{2+}_{(aq)} + 2e^- & \rightleftharpoons \text{Cu}_{(s)} \quad E^o = +0.34 \text{ v}
\end{align*}
\]

The more negative the \( E^o \) value, the further the position of equilibrium lies to the left. Remember that this is always relative to the hydrogen equilibrium - and not in absolute terms.

The negative sign of the zinc \( E^o \) value shows that it releases electrons more readily than hydrogen does. The positive sign of the copper \( E^o \) value shows that it releases electrons less readily than hydrogen.

Whenever you link two of these equilibria together, **electrons flow from one equilibrium with more negative standard electrode potential to the other less negative (more positive) standard electrode potential**. That upsets the equilibria, and Le Chatelier's Principle applies. The positions of equilibrium move - and keep on moving if the electrons continue to be transferred.
Will magnesium react with dilute sulphuric acid?

\[
\begin{align*}
\text{Mg}^{2+}_{(aq)} & + 2e^- & \rightarrow & \text{Mg}_{(s)} & \quad E^\circ = -2.37 \text{ v} \\
2\text{H}^+_{(aq)} & + 2e^- & \rightarrow & \text{H}_2_{(g)} & \quad E^\circ = 0 \text{ v}
\end{align*}
\]
REDOX POTENTIALS

Will magnesium react with dilute sulphuric acid?

You are starting with magnesium metal and hydrogen ions in the acid. The sulphate ions are spectator ions and play no part in the reaction.

This is the more negative value, so this equilibrium moves to the left.

This is the more positive (less negative) value, so this equilibrium moves to the right.
REDOX POTENTIALS

Will copper react with dilute sulphuric acid?

\[
\begin{align*}
\text{Cu}^{2+} & \quad + \quad 2e^- \quad \leftrightarrow \quad \text{Cu} \\
2\text{H}^+ & \quad + \quad 2e^- \quad \leftrightarrow \quad \text{H}_2
\end{align*}
\]

\[
\begin{align*}
\text{E}^\circ & = +0.34 \text{ v} \\
\text{E}^\circ & = 0 \text{ v}
\end{align*}
\]
REDOX POTENTIALS

Will copper react with dilute sulphuric acid?

It won't. How do the $E^\circ$ values predict this?

If we start from copper metal, the copper equilibrium is already completely to the right. If it were to react at all, the equilibrium will have to move to the left - directly opposite to what the $E^\circ$ values are saying.

Similarly, if we start from hydrogen ions (from the dilute acid), the hydrogen equilibrium is already as far to the left as possible. For it to react, it would have to move to the right - against what the $E^\circ$ values demand.

There is no possibility of a reaction.
REDOX POTENTIALS

Will oxygen oxidise iron(II) hydroxide to iron(III) hydroxide under alkaline conditions?

$$\begin{align*}
\text{Fe(OH)}_3(s) + e^- & \rightleftharpoons \text{Fe(OH)}_2(s) + \text{OH}^-_{(aq)} & E^\circ = -0.56 \text{ v} \\
\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- & \rightleftharpoons 4\text{OH}^-_{(aq)} & E^\circ = +0.40 \text{ v}
\end{align*}$$
REDOX POTENTIALS

Will oxygen oxidise iron(II) hydroxide to iron(III) hydroxide under alkaline conditions?

\[
\begin{align*}
\text{Fe(OH)}_3(s) + e^- & \rightleftharpoons \text{Fe(OH)}_2(s) + \text{OH}^-_{aq} & E^\circ &= -0.56 \text{ v} \\
\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- & \rightleftharpoons 4\text{OH}^-_{aq} & E^\circ &= +0.40 \text{ v}
\end{align*}
\]

Remember that the equilibrium with the more negative \( E^\circ \) value will tend to move to the left. The other one tends to move to the right.

Yes, it is possible.
REDOX POTENTIALS

Will chlorine oxidise manganese(II) ions to manganate(VII) ions?

\[ \text{MnO}_4^{-}(aq) + 8\text{H}^+(aq) + 5e^- \rightleftharpoons \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l) \quad E^\circ = +1.51 \text{ V} \]

\[ \text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq) \quad E^\circ = +1.36 \text{ V} \]
REDOX POTENTIALS

Will chlorine oxidise manganese(II) ions to manganate(VII) ions?

The manganese equilibrium has the more positive $E^\circ$ value and so will tend to move to the right. However, because we are starting from manganese(II) ions, it is already as far to the right as possible.

In order to get any reaction, the equilibrium would have to move to the left. That is against what the $E^\circ$ values are saying.

This reaction isn't feasible.
**REDOX POTENTIALS**

Will acidified potassium dichromate(VI) oxidise water?

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- & \rightleftharpoons 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l) \quad E^\circ = +1.33 \text{ V} \\
\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- & \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E^\circ = +1.23 \text{ V}
\end{align*}
\]

The relative sizes of the $E^\circ$ values show that the reaction is feasible.
REDOX POTENTIALS

Will acidified potassium dichromate(VI) oxidise water?

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- & \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E^\circ = +1.33 \text{ v} \\
\text{O}_2(g) + 4\text{H}^+ + 4e^- & \rightleftharpoons 2\text{H}_2\text{O(l)} \quad E^\circ = +1.23 \text{ v}
\end{align*}
\]

The relative sizes of the $E^\circ$ values show that the reaction is feasible.

However, in the test tube nothing happens however long you wait.

In fact, there is nothing wrong with the argument. The problem is that all the $E^\circ$ values show is that a reaction is possible.

They don't tell you that it will actually happen. There may be very large activation barriers to the reaction which prevent it from taking place.

Thermodynamics vs. kinetics
REDOX POTENTIALS

Will acidified potassium dichromate(VI) oxidise chloride ions to chlorine?

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-}(aq) & + 14\text{H}^+(aq) + 6\text{e}^- & \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l) & E^\circ = +1.33 \text{ v} \\
\text{Cl}_2(g) + 2\text{e}^- & \rightarrow 2\text{Cl}^{-}(aq) & E^\circ = +1.36 \text{ v}
\end{align*}
\]

Because the chlorine $E^\circ$ value is slightly greater than the dichromate(VI) one, there shouldn't be any reaction.
**REDOX POTENTIALS**

Potassium dichromate(VI) solution *does* oxidise concentrated hydrochloric acid to chlorine. The hydrochloric acid serves as the source of the hydrogen ions in the dichromate(VI) equilibrium and of the chloride ions.

E° values only apply under *standard* conditions. If you change the conditions you will change the position of an equilibrium - and that will change its E value. (Notice that you can't call it an E° value any more, because the conditions are no longer standard.)

The standard condition for concentration is 1 mol dm⁻³. But concentrated hydrochloric acid is approximately 10 mol dm⁻³. The concentrations of the hydrogen ions and chloride ions are far in excess of standard.

What effect does that have on the two positions of equilibrium?

![Chemical equations and reactions](image)
Nernst Equation

\[ O + ne = R \]

\[ E = E^o - (RT/nF) \left( \frac{a_R}{a_O} \right) , \quad E^o = ? \]

\[ E = E^{o'} - (RT/nF) \left( \frac{C_R}{C_O} \right) , \quad E^{o'} = \text{formal potential} \]

If the system follows the Nernst equation, the electrode reaction is often said to be thermodynamically or electrochemically reversible (or nernstian).

Reversibility of a process; one’s ability to detect the signs of disequilibrium

Rate of change of force driving the observed process vs. speed with which the system can reestablish equilibrium

If the perturbation applied to the system is small enough, or if the system can attain equilibrium rapidly enough compared to the measuring time, thermodynamic relation will apply.
Electrochemical Cell

Anion: -ve ion
Cation: +ve ion
Anode: electrode for oxidation reaction
Cathode: electrode for reduction reaction
Galvanic or Voltaic cells

Chemical reaction: material transformation
Electrochemical reaction: material transformation and electron flow

Galvanic cell: electron as a product
Use a chemical reaction (material transformation) to generate electrical energy
Ex) discharging of a secondary battery

Electrolytic cell: electron as a reactant
Use electrical energy to drive a chemical reaction (material transformation)
Ex) Charging of a secondary battery
Electrochemical Cell: Galvanic cell

Zn → Zn^{2+} + 2e
Electron generation
Anodic oxidation

Cu^{2+} + 2e → Cu
Electron consumption
Cathodic reduction
Electrochemical Cell: Electrolytic cell

Zn$^{2+}$ + 2e $\rightarrow$ Zn
Electron consumption
Cathodic reduction

Cu $\rightarrow$ Cu$^{2+}$ + 2e
Electron generation
Anodic oxidation
Galvanic cell vs. Electrolytic cell

**Galvanic cell**

- **Electric load**
  - Current flow
  - Electron flow
- **Electrochemical cell** determines the polarity of electrodes.

  - **Zn** → **Zn^{2+} + 2e**
  - Electron generation
  - Anodic oxidation

  - **Cu^{2+} + 2e** → **Cu**
  - Electron consumption
  - Cathodic reduction

**Electrolytic cell**

- **DC power supply**
  - Current flow
  - Electron flow
- **Electrochemical cell** determines the polarity of electrodes.

  - **Zn^{2+} + 2e** → **Zn**
  - Electron consumption
  - Cathodic reduction

  - **Cu** → **Cu^{2+} + 2e**
  - Electron generation
  - Anodic oxidation

**Zinc sulphate solution** [Zn^{2+}] = 1 mol dm^{-3}

**Copper(II) sulphate solution** [Cu^{2+}] = 1 mol dm^{-3}
Galvanic or Voltaic cells

Electrochemical cells that use an oxidation-reduction reaction to generate an electric current are known as **galvanic** or **voltaic cells**. Because the potential of these cells to do work by driving an electric current through a wire is measured in units of volts, we will refer to the cells that generate this potential from now on as **voltaic cells**.

The cell potential for a voltaic cell is literally the potential of the cell to do work on its surroundings by driving an electric current through a wire.

Electrons travel from the anode, around the external circuit and to the cathode. The electrons pushed around the external circuit can do work (run a motor, illuminate a light bulb, etc.).

The amount of work possible is a function of both the voltage (potential) and of the current (number of electrons) in the circuit.

Pushing one Coulomb of charge around a circuit at a potential of 1 Volt does one Joule of work.

Or, mathematically, \( 1J = 1V \times 1C \).
Galvanic or Voltaic cells

By definition, one joule of energy is produced when one coulomb of electrical charge is transported across a potential of one volt.

\[ 1 \ V = \frac{1 \ J}{1 \ C} \]

The potential of a voltaic cell depends on the concentrations of any species present in solution, the partial pressures of any gases involved in the reaction, and the temperature at which the reaction is run.

**standard-state conditions**

- All solutions are 1 M.
- All gases have a partial pressure of 1 bar (0.1 MPa or 0.9869 atm)
- Measurement temperature of 25° C
The first law of thermodynamics

The total energy of a system: Internal energy, $U$

The absolute value of the total energy of a system cannot be known.

For an isolated system, the total energy of the system remains constant.

For an isolated system, $\Delta U = 0$  \hspace{1cm} (2.10)

For an infinitesimal change, $dU = 0$

When the total energy of a system changes, the energy change goes into either work or heat.

$$\Delta U = q + w$$ \hspace{1cm} (2.11)

The change in the internal energy for a process is equal to the work plus the heat involved during the process.

Heat flow into the system: $+ve$, heat flow out of the system: $-ve$
Work \[ \Delta U = q + w \] \hspace{1cm} (2.11)

\[ w_{\text{system}} < 0 \] Work is done by the system on the surroundings.

\[ w_{\text{system}} > 0 \] Work is done on the system by the surroundings.

There are a number of different kinds of work which can be done by or on a thermodynamic system during a change in its state. Some common examples are given in the table below.

<table>
<thead>
<tr>
<th>kind of work</th>
<th>expression for ( dw )</th>
</tr>
</thead>
<tbody>
<tr>
<td>lifting a mass ( m ) a distance ( dh )</td>
<td>( dw = -mgdh )</td>
</tr>
<tr>
<td>a system increasing its volume by ( dV ) against an opposing pressure ( p_{\text{ex}} )</td>
<td>( dw = -p_{\text{ex}}dV )</td>
</tr>
<tr>
<td>a system increasing its surface area by ( dA ) against a surface tension ( \gamma )</td>
<td>( dw = -\gamma dA )</td>
</tr>
<tr>
<td>stretching a wire by ( dl ) against a tensile force ( f )</td>
<td>( dw = -fdl )</td>
</tr>
<tr>
<td>causing ( dq ) coulombs of charge to flow through a potential difference ( \varepsilon )</td>
<td>( dw = -\varepsilon dq )</td>
</tr>
</tbody>
</table>
Free Energy

\[ \Delta U = q + w, \quad dU = dq + dw \quad (2.11) \]

We can now use the Second Law together with the definitions of \( A \) and \( G \) to derive alternative criteria for spontaneity.

The Second Law tells us that for any infinitesimal thermodynamic process,

\[ dS \geq \frac{dq}{T} \]

where the inequality holds for a spontaneous (irreversible) process and the equality holds for a reversible process. Rearranging this relation and substituting for \( dq \), we obtain

\[ TdS \geq dq = dU - dw = dU + p_{ex} dV - dW_{net}. \]

\[ dW = -P_{ext} dV + dW_{net} \]

For a closed system of fixed composition, then, we have the perfectly general relationship

\[ TdS - dU - p_{ex} dV + dW_{net} \geq 0. \quad (1) \]
Gibbs Free Energy

\[ G = H - TS \]
\[ dG = dH - d(TS) = dH - TdS - SdT. \]

The Second Law tells us that for any infinitesimal thermodynamic process,

\[ dS \geq \frac{dq}{T} \]

where the inequality holds for a spontaneous (irreversible) process and the equality holds for a reversible process. Rearranging this relation and substituting for \( dq \), we obtain

\[ TdS \geq dq = dU - dw = dU + p_{ex}dV - dw_{net}. \]

For a closed system of fixed composition, then, we have the perfectly general relationship

\[ TdS - dU - p_{ex}dV + dw_{net} \geq 0. \] (1)

On the other hand, for a process at constant \( T \) and \( p = p_{ex} \),

\[ dG = dH - TdS \]
\[ = dU + p_{ex}dV - TdS \]

and Eqn. 1 becomes

\[ -dG + dw_{net} \geq 0 \quad \text{or} \quad -dG \geq -dw_{net} \]

If the system does no net work,

\[ -dG \geq 0 \quad \text{or} \quad dG \leq 0 \]
Gibbs Free Energy

On the other hand, for a process at constant $T$ and $p = p_{ex}$,

$$dG = dH - TdS$$

$$= dU + p_{ex}dV - TdS$$

and Eqn. 1 becomes

$$-dG + dw_{net} \geq 0 \quad \text{or} \quad -dG \geq -dw_{net}$$

If the system does no net work,

$$-dG \geq 0 \quad \text{or} \quad dG \leq 0$$

and $\Delta G$ must be $< 0$ for a spontaneous process and equal to 0 for a reversible process. Under these conditions, any spontaneously occurring change of state will decrease the free energy $G$ of the system, and when all spontaneous changes stop and the system is in equilibrium, $G$ will be a minimum. Thus we have our second alternative criterion for spontaneity and equilibrium:

For a thermodynamic transformation at constant $T$ and $p$ in a closed system of constant composition in which no net work is done, \( \begin{cases} \Delta G < 0 \\ \Delta G = 0 \end{cases} \) for a \( \begin{cases} \text{spontaneous} \\ \text{reversible} \end{cases} \) process and the criterion for equilibrium is that $dG = 0$ or $G$ is a minimum.
Gibbs Free Energy

On the other hand, for a process at constant $T$ and $p = p_{\text{ex}}$,

$$dG = dH - TdS$$

$$= dU + p_{\text{ex}}dV - TdS$$

and Eqn. 1 becomes

$$- dG + dw_{\text{net}} \geq 0 \quad \text{or} \quad - dG \geq - dw_{\text{net}}$$

$$dW = - P_{\text{ext}} dV + dW_{\text{net}}$$

We also saw that $- dG \geq - dw_{\text{net}}$ for an isothermal, constant-pressure infinitesimal process. Therefore, $- \Delta G$ is the maximum amount of net or useful work a closed system of constant composition can do during a thermodynamic process at constant $T$ and $p$ and this maximum work is achieved when the process is carried out reversibly. $G$ is, in fact, called the free energy because $- \Delta G$ is the maximum amount of energy available or free to do useful work during an isothermal, constant-pressure process. Similarly, $A$ is called the free energy because $- \Delta A$ is the maximum amount of energy available or free to do useful work during an isothermal, constant-volume process (when $w_{pv} = 0$).
Gibbs Free Energy

On the other hand, for a process at constant $T$ and $p = p_{ex}$,

$$dG = dH - TdS$$

$$= dU + p_{ex}dV - TdS$$

and Eqn. 1 becomes

$$-dG + dw_{net} \geq 0 \quad \text{or} \quad -dG \geq -dw_{net}$$

$$dW = -P_{ext}dV + dW_{net}$$

| causing $dq$ coulombs of charge to flow through a potential difference $\varepsilon$ | $dw = -\varepsilon dq$ |

At equilibrium, $dG = dW_{net} = -E\ dq$

| $w_{system} < 0$ | Work is done by the system on the surroundings. |
| $w_{system} > 0$ | Work is done on the system by the surroundings. |
Nernst Equation

$dq$ coulombs of charge to flow through a potential difference $\varepsilon$

At equilibrium, $dG = dW_{\text{net}} = -E \ dq$

In materials electrochemistry, work done by the system on the surrounding in transferring $n$ moles of electrons across a potential difference $E$ is expressed as a positive work

$dG = -[E (-nF)]$

<table>
<thead>
<tr>
<th>equilibrium</th>
<th>$E^\circ$ (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}^+<em>{(aq)} + e^- \rightarrow \text{Li}</em>{(s)}$</td>
<td>$-3.03$</td>
</tr>
<tr>
<td>$\text{K}^+<em>{(aq)} + e^- \rightarrow \text{K}</em>{(s)}$</td>
<td>$-2.92$</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}<em>{(aq)} + 2e^- \rightarrow \text{Ca}</em>{(s)}$</td>
<td>$-2.87$</td>
</tr>
<tr>
<td>$\text{Na}^+<em>{(aq)} + e^- \rightarrow \text{Na}</em>{(s)}$</td>
<td>$-2.71$</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}<em>{(aq)} + 2e^- \rightarrow \text{Mg}</em>{(s)}$</td>
<td>$-2.37$</td>
</tr>
<tr>
<td>$\text{Al}^{3+}<em>{(aq)} + 3e^- \rightarrow \text{Al}</em>{(s)}$</td>
<td>$-1.66$</td>
</tr>
<tr>
<td>$\text{Zn}^{2+}<em>{(aq)} + 2e^- \rightarrow \text{Zn}</em>{(s)}$</td>
<td>$-0.76$</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}<em>{(aq)} + 2e^- \rightarrow \text{Fe}</em>{(s)}$</td>
<td>$-0.44$</td>
</tr>
<tr>
<td>$\text{Pb}^{2+}<em>{(aq)} + 2e^- \rightarrow \text{Pb}</em>{(s)}$</td>
<td>$-0.13$</td>
</tr>
<tr>
<td>$2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_2(g)$</td>
<td>$0$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}<em>{(aq)} + 2e^- \rightarrow \text{Cu}</em>{(s)}$</td>
<td>$+0.34$</td>
</tr>
<tr>
<td>$\text{Ag}^+<em>{(aq)} + e^- \rightarrow \text{Ag}</em>{(s)}$</td>
<td>$+0.80$</td>
</tr>
<tr>
<td>$\text{Au}^{3+}<em>{(aq)} + 3e^- \rightarrow \text{Au}</em>{(s)}$</td>
<td>$+1.50$</td>
</tr>
</tbody>
</table>

From the above, it should be apparent that the potential difference between the electrodes of a cell is a measure of the tendency for the cell reaction to take place: the more positive the cell potential, the greater the tendency for the reaction to proceed to the right. But we already know that the standard free energy change, $\Delta G^\circ$, expresses the tendency for any kind of process to occur under the conditions of constant temperature and pressure. Thus $E^\circ$ and $\Delta G^\circ$ measure the same thing, and are related in a simple way:

$$\Delta G^\circ = -nFE^\circ$$  \hspace{1cm} (8)
Nernst Equation

\[ \Delta G^\circ = -nFE^\circ \] (8)

A few remarks are in order about this very fundamental and important relation:

- The negative sign on the right indicates that a positive cell potential (according to the sign convention discussed previously) implies a negative free energy change, and thus that the cell reaction will proceed to the right.

- *Electrical work* is done when an electric charge \( q \) moves through a potential difference \( \Delta V \). The right side of Eq 8 refers to the movement of \( n \) moles of charge across the cell potential \( E^\circ \), and thus has the dimensions of work.

- The Gibbs function is more than a criterion for spontaniety; the value of \( \Delta G^\circ \) expresses the maximum useful work that a system can do on the surroundings. “Useful” here means work other than \( P-V \) work that is simply a consequence of volume change, which cannot be channelled to some practical use. This maximum work can only be extracted from the system under the limiting conditions of a reversible change, which for an electrochemical cell, implies zero current. The more rapidly the cell operates, the less electrical work it can supply.

- If \( F \) is expressed in coulombs per mole, the electrical work \( \Delta G^\circ \) is in joules per mole. To relate these units to electrical units, recall that the coulomb is one amp-sec, and that *power*, which is the *rate* at which work is done, is measured in *watts*, which is the product of amps and volts. Thus

\[
1 \text{ J} = 1 \text{ watt-sec} = 1 \text{ (amp-sec)} \times \text{ volts}
\]
**Electrochemical potentials**

Electrochemical potential for species $i$ with charge $z_i$ in phase $\alpha$

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F \Phi^\alpha$$

Chemical potential, $\mu_i^\alpha = (\partial G / \partial n_i)_{n_j \neq i, P, T}$

Electrochemical potential, $\bar{\mu}_i^\alpha = (\partial \bar{G} / \partial n_i)_{T, P, n_j \neq i}$

$\bar{G}$: electrochemical free energy

(a) Properties of electrochemical potential

1. For an uncharged species: $\bar{\mu}_i^\alpha = \mu_i^\alpha$
2. For any substance: $\mu_i^\alpha = \mu_i^{0\alpha} + RT / n_i \alpha$, where $\mu_i^{0\alpha}$ is the standard chemical potential, and $a_i$ is the activity
3. For a pure phase at unit activity (e.g., solid Zn, AgCl, Ag, H$_2$): $\bar{\mu}_i^\alpha = \mu_i^{0\alpha}$
4. For electrons in a metal ($z = -1$): $\bar{\mu}_e^\alpha = \mu_e^{0\alpha} - F \Phi^\alpha$
5. For an equilibrium of species $i$ between phase $\alpha$ and $\beta$: $\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta$
Cu(s) + 2 Ag⁺(aq) = Cu²⁺(aq) + 2 Ag(s), \( E^o = 0.46 \text{ V} \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) )</td>
<td>+0.34 V</td>
</tr>
<tr>
<td>( Ag^+(aq) + e^- \rightarrow Ag(s) )</td>
<td>+0.80 V</td>
</tr>
</tbody>
</table>

Anodic oxidation
Cathodic Reduction

Cu/Cu²⁺//Ag⁺/Ag/Cu' or Ag'/Cu/Cu²⁺//Ag⁺/Ag

Cathode half cell rxn: \( Ag^+ + e^- (Cu') = Ag \)
Anode half cell rxn: \( Cu^{2+} + 2e^- (Cu) = Cu \)
Note that all half cell rxns are written in reduction rxn.

Overall unit cell rxn = [Cathode half cell rxn] – [Anode half cell rxn]
Unit cell voltage = [Cathode half cell rxn potential] – [Anode half cell rxn potential]
\( 2Ag^+ + 2e^- (Cu') + Cu = 2Ag + Cu^{2+} + 2e^- (Cu) \)

Electrochemical equilibrium?
\[ \text{Cu(s) + 2 \text{Ag}^+(aq) = Cu}^{2+}(aq) + 2 \text{Ag(s)}, \text{E}^0 = 0.46 \text{ V} } \]

\[ \text{Cu/Cu}^{2+}//\text{Ag}^+/\text{Ag/Cu'} \]

Overall unit cell rxn = [Cathode half cell rxn] – [Anode half cell rxn]

Unit cell voltage = [Cathode half cell rxn potential] – [Anode half cell rxn potential]

\[ 2\text{Ag}^+ + 2e \ (\text{Cu'}) + \text{Cu} = 2\text{Ag} + \text{Cu}^{2+} + 2e \ (\text{Cu}) \]

Electrochemical equilibrium: 

\[ 2\mu_{\text{Ag}^+}^s + 2\mu_{\text{Cu}}' + \mu_{\text{Cu}}^s\text{Cu} = 2\mu_{\text{Ag}^+} + \mu_{\text{Cu}^{2+}}^s + 2\mu_e' \]

\[ 2(\mu_{\text{Cu}}' - \mu_{\text{Cu}}^s) = 2[(\mu_{\text{Cu}}' - F\phi_{\text{Cu}'}) - (\mu_{\text{Cu}}^s - F\phi_{\text{Cu}})] \]

\[ = -2F[\phi_{\text{Cu}'} - \phi_{\text{Cu}}] = -2FE \]

\[ 2\mu_{\text{Ag}^+} + \mu_{\text{Cu}^{2+}}^s - 2\mu_{\text{Ag}^+}^s - \mu_{\text{Cu}}^s\text{Cu} \]

\[ = 2\mu_{\text{Ag}^+}^{o,\text{Ag}} + (\mu_{\text{o,Cu}^{2+}}^s + RT/n \ a_{\text{Cu}^{2+}} + 2F\phi_s) \]

\[ - 2(\mu_{\text{Ag}^+}^{o,\text{Ag}} + RT/n \ a_{\text{Ag}} + F\phi_s) - \mu_{\text{o,\text{Cu}}^{s}}^s\text{Cu} \]

\[ = 2\mu_{\text{Ag}^+}^{o,\text{Ag}} + \mu_{\text{o,\text{Cu}^{2+}}}^s - 2\mu_{\text{Ag}^+}^{o,s} - \mu_{\text{o,\text{Cu}}}^{s,\text{Cu}} + RT/n \ a_{\text{Cu}^{2+}} - 2RT/n \ a_{\text{Ag}} \]

\[ = \Delta G^0 + RT/n \ [a_{\text{Cu}^{2+}}/(a_{\text{Ag}})^2] \]

\[ -2F[\phi_{\text{Cu}'} - \phi_{\text{Cu}}] = -2FE = \Delta G^0 + RT/n \ [a_{\text{Cu}^{2+}}/(a_{\text{Ag}})^2] \]

\[ \text{E} = \Delta G^0/(2F) - (RT/2F)/n \ [a_{\text{Cu}^{2+}}/(a_{\text{Ag}})^2] \]

\[ = \text{E}^0 - (RT/2F)/n \ [a_{\text{Cu}^{2+}}/(a_{\text{Ag}})^2] \]
Chemical Equilibrium in Gas Phase Mixture

Le Chatelier’s Principle

Le Chatelier’s Principle, for pressure:

An increase in pressure shifts the equilibrium so as to decrease the total # of moles, reducing the volume.

In the example above, increasing $p$ shifts the equilibrium toward the reactants.

LeChatlier’s Principle states that a system at equilibrium when stressed (a stress could be an increase or decrease in temperature, pressure, volume, number of moles of reactants or products, etc.) will establish a new equilibrium in a way that will reduce the applied stress.
**Nernst Equation**

**Nernst equation** for an electrode reaction of \( O + ne = R \) as:

\[
\Delta G = \Delta G^0 + RT \ln \left( \frac{a_{(Reductant)}}{a_{(Oxidant)}} \right)
\]

\[-\Delta G = zF\Delta E, \quad -\Delta G^0 = zF\Delta E^0\]

\[
E = E^0 - \left( \frac{RT}{nF} \right) \ln \left( \frac{a_{(Reductant)}}{a_{(Oxidant)}} \right)
\]

where \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( n \) is the charge number of the electrode reaction (which is the number of moles of electrons involved in the reaction as written), and \( F \) is the Faraday constant. The charge on a mole of electrons can be calculated from Avogadro's number and the charge on a single electron.

\[
\frac{6.022045 \times 10^{23} \text{ e}^-}{1 \text{ mol}} \times \frac{1.6021892 \times 10^{-19} \text{ C}}{1 \text{ e}^-} = 96,484.56 \text{ C/mol}
\]

\[
E = E^0 - (0.02568/n) \ln \left( \frac{a_{(Reductant)}}{a_{(Oxidant)}} \right)
\]

As \( a_{(Reductant)} \) increases, \( E \) decreases. (or increases to –ve direction)

As \( a_{(Oxidant)} \) increases, \( E \) increases. (or increases to +ve direction)
For the Daniel cell at 25°C, \( \text{Zn} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu} \)

What happen to the cell potential as the reaction proceeds?

\[
E = E^* - \frac{0.02568}{2} \ln \left( \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)
\]

When the reaction quotient is very small, the cell potential is positive and relatively large, because the reaction is far from **equilibrium** and the driving force behind the reaction should be relatively large.

When the reaction quotient is very large, the cell potential is negative. This means that the reaction would have to shift back toward the reactants to reach **equilibrium**.
Nernst Equation

Consider the following set of half-reactions

**Cathode**  \[ \text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe} \quad E_{\text{red}}^\circ = -0.44 \text{ V} \]

**Anode**  \[ \text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn} \quad E_{\text{ox}}^\circ = -0.76 \text{ V} \]

**Overall**  \[ \text{Zn} + \text{Fe}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Fe} \quad E_{\text{cell}}^\circ = 0.32 \text{ V} \]

This is valid only if all species have concentrations of 1 M.

What if not all the species are at Standard Conditions?
Nernst Equation

Overall \[ \text{Zn} + \text{Fe}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Fe} \] \( E_{\text{cell}} = 0.32 \text{ V} \)

This is valid only if all species have concentrations of 1 M.

What if not all the species are at Standard Conditions?

Le Châtelier's principle gives us some ideas. Consider the reaction to be at equilibrium If we add more \( \text{Fe}^{2+} \) to the reaction mixture, the equilibrium will shift to the right to use up the excess \( \text{Fe}^{2+} \). This will, of course, cause a positive cell potential to be measurable.

Conversely, if we removed \( \text{Fe}^{2+} \) from the reaction mixture, the equilibrium would shift to the left to try to replace some of the missing \( \text{Fe}^{2+} \). This would result in a measurable negative potential (reaction goes left).

So, if we add \( \text{Fe}^{2+} \) to a mixture at Standard Conditions, then the voltage would be more positive and if we removed some \( \text{Fe}^{2+} \) from a mixture at Standard Conditions the measured voltage would be lower (less positive).

The reverse results would be found for addition or removal of \( \text{Zn}^{2+} \) (a product). More \( \text{Zn}^{2+} \) would give a lower positive potential and \textit{vice versa}. 
**Nernst Equation**

We can calculate the voltage for the situation where the concentrations are not standard. For example, consider $[\text{Fe}^{2+}] = 0.1 \, M$ and $[\text{Zn}^{2+}] = 1.9 \, M$.

For this reaction, we also know that there are two electrons transferred for each equation ($n = 2$).

\[
E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]}
\]

\[
= 0.32 \, V - \frac{8.3145 \frac{J}{\text{mol} \cdot \text{K}} \times 298.15 \text{K}}{2 \times 96485 \frac{\text{C}}{\text{mol}}} \ln \frac{1.9}{0.10}
\]

\[
= 0.28 \, V
\]

Although the reaction is 90% complete (from Standard Conditions initial) the cell potential has only dropped by a small amount (0.04 V). This is normal. For example, the batteries in your flashlight will put out almost full voltage until the last traces of chemical are almost used up at which point the voltage will drop off rather sharply. This is an especially useful characteristic of cells powering electronic equipment, (like a calculator or CD player, etc.) which require a certain minimum (and dependable) voltage to operate successfully.
17.11 KINDS OF ELECTRODES

At this point we describe briefly some important kinds of electrodes, and present the half-cell reactions and the Nernst equation for each.

17.11.1 Gas–Ion Electrodes

The gas–ion electrode consists of an inert collector of electrons, such as platinum or graphite, in contact with a gas and a soluble ion. The $H_2\mid H^+$ electrode, discussed in detail in Section 17.8, is one example. Another example is the chlorine electrode, $Cl_2\mid Cl^-\mid graphite$:

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad \phi = \phi^o - \frac{RT}{2F} \ln \frac{a_{Cl^-}^2}{p_{Cl_2}} \quad (17.46)$$

The hydrogen electrode is illustrated in Fig. 17.2. Purified hydrogen gas is passed over a platinum electrode which is in contact with an acid solution. At the electrode surface the equilibrium

$$H^+(aq) + e^-(Pt) \rightleftharpoons \frac{1}{2}H_2(g)$$

$$\phi_{H^+\mid H_2} = \phi^o_{H^+\mid H_2} - \frac{RT}{F} \ln \frac{f^{1/2}}{a_{H^+}}.$$

The hydrogen electrode is illustrated in Fig. 17.2. Purified hydrogen gas is passed over a platinum electrode which is in contact with an acid solution. At the electrode surface the equilibrium

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

\[ \phi_{\text{H}^+/\text{H}_2} = \phi_{\text{H}^+/\text{H}_2}^\circ - \frac{RT}{F} \ln \frac{f^{1/2}_{\text{H}_2}}{a_{\text{H}^+}} \]

![Diagram of the hydrogen electrode](image)

**Figure 17.2** The hydrogen electrode.
17.11.2 Metal Ion–Metal Electrodes

The electrode consists of a piece of the metal immersed in a solution containing the metal ion. The $\text{Zn}^{2+} | \text{Zn}$ and $\text{Cu}^{2+} | \text{Cu}$ electrodes described earlier are examples.

\[
\text{M}^{n+} + n\text{e}^- \rightleftharpoons \text{M} \quad \phi = \phi^o - \frac{RT}{nF} \ln \frac{1}{a_{\text{M}^{n+}}} \quad (17.47)
\]

17.11.3 Metal–Insoluble Salt-Anion Electrodes

This electrode is sometimes called an “electrode of the second kind.” It consists of a bar of metal immersed in a solution containing a solid insoluble salt of the metal and anions of the salt. There are a dozen common electrodes of this kind; we cite only a few examples.

The Silver–Silver Chloride Electrode. $\text{Cl}^- | \text{AgCl(s)} | \text{Ag(s)}$: (Fig. 17.3).

\[
\text{AgCl(s)} + \text{e}^- \rightleftharpoons \text{Ag(s)} + \text{Cl}^-(\text{aq}) \quad \phi = \phi^o - \frac{RT}{F} \ln a_{\text{Cl}^-} \quad (17.48)
\]

The activity of AgCl does not appear in the quotient, since AgCl is a pure solid. Since the potential is sensitive to the concentration of chloride ion, it can be used to measure that concentration. The silver–silver chloride electrode is a very commonly used reference electrode.

A number of commonly used reference electrodes based on mercury belong to this class of electrodes.
The Silver–Silver Chloride Electrode. $\text{Cl}^-|\text{AgCl}(s)|\text{Ag}(s)$: (Fig. 17.3).

$$\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-(aq) \quad \phi = \phi^o - \frac{RT}{F} \ln a_{\text{Cl}^-} \quad (17.48)$$

The activity of AgCl does not appear in the quotient, since AgCl is a pure solid. Since the potential is sensitive to the concentration of chloride ion, it can be used to measure that concentration. The silver–silver chloride electrode is a very commonly used reference electrode.

![Figure 17.3 Silver–silver chloride electrode.](image)
The Calomel Electrode. A pool of mercury covered with a paste of calomel (mercurous chloride) and a solution of KCl.

\[
\text{Hg}_2\text{Cl}_2(\text{s}) + 2e^- \rightleftharpoons 2\text{Hg(l)} + 2\text{Cl}^- (\text{aq}) \quad \phi = \phi^\circ - \frac{RT}{2F} \ln a_{\text{Cl}^-}^2.
\]


\[
\text{HgO(s)} + \text{H}_2\text{O(l)} + 2e^- \rightleftharpoons \text{Hg(l)} + 2\text{OH}^- (\text{aq}) \quad \phi = \phi^\circ - \frac{RT}{2F} \ln a_{\text{OH}^-}^2.
\]


\[
\text{Hg}_2\text{SO}_4(\text{s}) + 2e^- \rightleftharpoons 2\text{Hg(l)} + \text{SO}_4^{2-} (\text{aq}) \quad \phi = \phi^\circ - \frac{RT}{2F} \ln a_{\text{SO}_4^{2-}}.
\]
17.11.4 "Oxidation–Reduction" Electrodes

Any electrode involves oxidation and reduction in its operation, but these electrodes have had that superfluous phrase attached to them. An oxidation–reduction electrode has an inert metal collector, usually platinum, immersed in a solution that contains two soluble species in different states of oxidation. An example is the ferric–ferrous ion electrode (Fig. 17.4):

\[ \text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} \quad \phi = \phi^0 - \frac{RT}{F} \ln \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} \]  

(17.49)

Figure 17.4 The ferric–ferrous electrode.