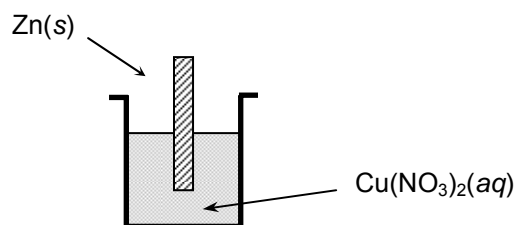


Electrochemical cells

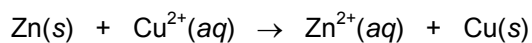
In this chapter, we turn our attention to electron transfer reactions.

To identify an electron transfer reactions, we must assign oxidation states – review rules in Chapter 3.

e.g.



A copper coating forms spontaneously on the zinc rod because of the following reaction.



All oxidation-reduction reactions can be “split” into two separate half-reactions.

oxidation:

reduction:

overall:

In this particular example, the electron transfer is “direct” in the sense that the reactants are in direct contact with each other. The interesting (and useful) thing about electron transfer reactions is that they can be carried out even if the reactants are not in direct contact!

Electrochemical cells

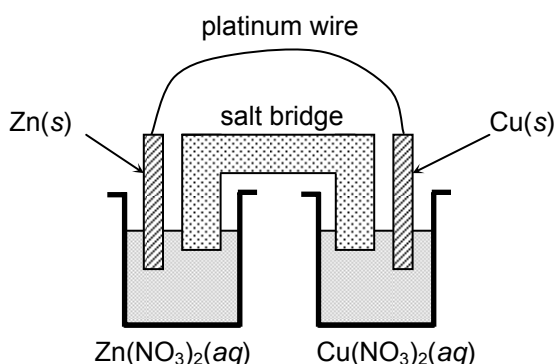
- the reactants are physically separated but are electrically connected by a **conducting material**
- made up of two "**half-cells**" and a **salt bridge**

Electrons flow through conducting materials (e.g. Pt wire, Cu wire, etc.)

An electrode immersed in a solution. An electrode is a solid that provides the surface for the electron transfer.

A tube filled with concentrated salt solution.

The reaction between Zn(s) and $\text{Cu}^{2+}(\text{aq})$ could be carried out using the following set up.



In this example, the zinc electrode is the **anode** and the copper electrode is the **cathode**.

anode = **electrode where oxidation occurs (left)**

cathode = **electrode where reduction occurs (right)**

An electrochemical cell can be classified as:

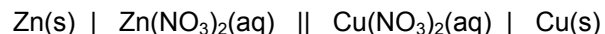
(1) galvanic or voltaic ↔ based on a spontaneous redox reaction

Galvanic cell produces energy – a battery is a galvanic cell

(2) electrolytic ↔ based on a non-spontaneous redox reaction

**Electrolytic cell requires/consumes energy –
electrolytic cells are important for converting metal
ions into metallic solids)**

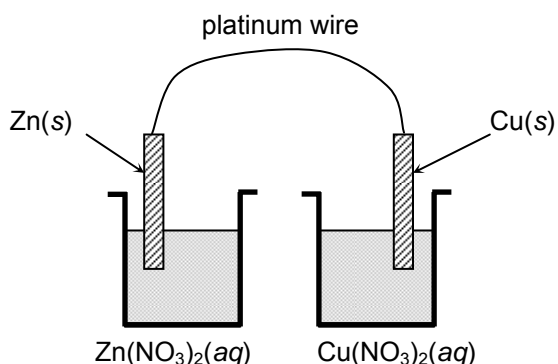
Chemists have devised a shorthand notation for describing the components making up an electrochemical cell. Using this notation, the electrochemical cell discussed previously is represented as:



What is the function of the salt bridge?

The salt bridge prevents “charge build-up” in the electrochemical cell.

Consider what happens in our electrochemical cell if the salt bridge is not there.



We would get a build-up of positive charge in one solution and a build-up of negative charge in the other solution.

With the salt bridge in place, the positive ions in the salt bridge migrate towards one end of the tube and some of them diffuse into the solution to offset the build up of negative charge that would otherwise occur in that solution. The negative ions in the salt bridge travel in the opposite direction.

By the end of this unit, you should be able to predict for any cell the direction of electron flow and the directions of ion migration in the salt bridge.

The Cell Potential

The “cell potential” is an important quantity to consider when dealing with electrochemical cells.

cell potential =

The cell potential depends on:

- (i) the oxidizing or reducing strength of each half-cell

- (ii) the conditions under which the cell operates

Our first concern is to investigate the oxidizing/reducing strengths of different half cells. In order to come up with a scale that ranks the oxidizing/reducing strengths of half-cells quantitatively, we must

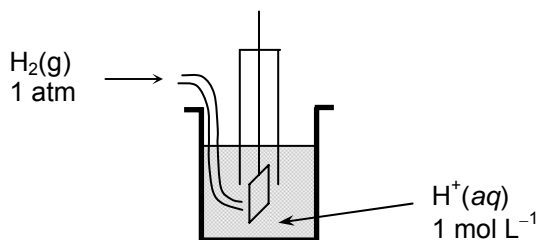
- fix the conditions

Standard conditions

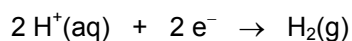
- compare all possible half-cells to an accepted reference half-cell

Standard hydrogen electrode (SHE) and standard electrode potentials

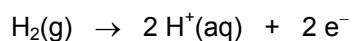
The basic construction of the standard hydrogen electrode is shown below.



The half-reactions associated with the SHE are:



If the SHE is the CATHODE.



If the SHE is the ANODE.

These two half-reactions are assigned a voltage of zero volts (for standard conditions).

We can use the following strategy to assign a voltage to other half-reactions.

- (1) Connect another half-cell to the SHE
- (2) Measure the cell potential (i.e. voltage) and determine the direction of electron flow.
- (3) Assign that voltage to the half-cell reaction using a “+” sign or a “-” sign.

Table of Standard Reduction Potentials

Half-reaction	E° / V
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	2.889
$\text{Au}^+(\text{aq}) + \text{e}^- \rightarrow \text{Au}(\text{s})$	1.691
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.512
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.229
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	1.078
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.799
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$	0.401
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.339
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	0.22
$\text{AgBr}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Br}^-(\text{aq})$	0.0732
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.0000
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.04
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.127
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.236
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Co}(\text{s})$	-0.282
$\text{Tl}^+(\text{aq}) + \text{e}^- \rightarrow \text{Tl}(\text{s})$	-0.336
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.402
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.41
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.762
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.809
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.00

Note carefully:

- all of the half-reactions in the table are written as reductions
- the E° value assigned to each half-reaction is the voltage we'd get if a half-cell based on that half-reaction was connected to the SHE

- the more positive the E° value, the greater the tendency of the reaction to occur as written
 - ⇒ when “coupling” two half-reactions, the half-reaction with the more positive E° value has a greater tendency to occur as a reduction.

Using standard reduction potentials to calculate E_{cell}°

The cell potential is equal to the energy transferred per unit of charge transferred:

With this in mind, it is straightforward to establish the following rules.

- If we reverse a half-reaction, then E° changes sign.
- If we multiply a half-reaction by “ n ”, then E° is unchanged.
- If we add two half-reactions together, then we add the two E° values.

We can use these rules, and a table of standard reduction potentials, to calculate E_{cell}° for any electrochemical cell.

Example: A galvanic cell is constructed using Pb/Pb²⁺ and Ag/Ag⁺ half-cells. The cell operates under standard conditions.

(a) Identify the anode and the cathode.

(b) Draw a diagram of the cell. What is the shorthand notation for the cell?

Show the direction of electron transfer. Which electrode increases in mass?

(c) What is E_{cell}° ?

A “different” way to calculate E_{cell}° ? Not really ...

In the previous example, we calculated E_{cell}° using the equation below.

$$E_{\text{cell}}^{\circ} = E_{\text{oxid}}^{\circ} + E_{\text{red}}^{\circ}$$

When we use the equation above, we are emphasizing that the overall reaction is the sum of an oxidation process and a reduction process, and that the cell potential is the sum of an oxidation potential and a reduction potential.

Your text book uses the following equation to calculate the cell potential:

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} .$$

In the equation above,

$E_{\text{cathode}}^{\circ} =$ **The reduction potential for the cathode reaction
(written as a reduction)**

$E_{\text{anode}}^{\circ} =$ **The reduction potential for the anode reaction
(written as a reduction)**

When we use the equation $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$, we are emphasizing that E_{cell}° depends on the difference between the **reducing strengths** of the two half-cells and that E_{cell}° is the difference between two **reduction** potentials.

Either one of these equations can be used to calculate E_{cell}° , provided you use the equations properly and understand the meaning of the terms involved.

What does the sign of E° tell us?

Armed with the formulae

$$E_{\text{cell}}^\circ = E_{\text{oxid}}^\circ + E_{\text{red}}^\circ \quad \text{and} \quad E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

we can calculate the value of E° for any oxidation-reduction reaction provided we know the reduction potentials for the two half-reactions.

The E° value for a given reaction can be positive or negative, and the sign of the E° value has the following interpretation. (We will justify this interpretation later.)

$E^\circ > 0 \Rightarrow$ Under standard conditions, the reaction proceeds spontaneously in the forward direction

$E^\circ < 0 \Rightarrow$ Under standard conditions, the reaction proceeds spontaneously in the reverse direction

$E^\circ = 0 \Rightarrow$ Under standard conditions, the reaction is at equilibrium.

Oxidizing and reducing agents

A table of standard reduction potentials can be used to identify oxidizing and reducing agents.

oxidizing agent ↔ **causes something else to be oxidized –
a good oxidizing agent is a substance
that is easily reduced**

reducing agent ↔ **causes something else to be reduced –
a good reducing agent is a substance
that is easily oxidized**

From the table of standard reduction potentials, we can see that:

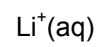
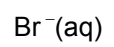
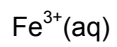
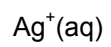
$F_2(g)$ is a strong oxidizing agent because ...

**$F_2(g)$ has a strong tendency to be reduced – i.e. it has a
very positive reduction potential**

$Na(s)$ is a strong reducing agent because ...

**$Na(s)$ has a very positive oxidation potential or a very
negative reduction potential**

Example: Which of the following substances most readily reduces Pb^{2+} to Pb under standard conditions?



The Nernst Equation

The Nernst equation can be used to understand how the cell potential changes with concentration.

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

The Nernst equation is obtained when you apply the laws of thermodynamics to electrochemical cells. The derivation of this equation requires discussion of the three laws of thermodynamics. Unfortunately, a meaningful discussion of the laws of thermodynamics is a course in itself, e.g. CHEM 254. We don't expect you to know where this equation comes from, but we do expect you to know how to use it. The Nernst equation will be supplied on the Data Sheet.

Important points to remember

(1) Q in the equation above is the "thermodynamic reaction quotient".

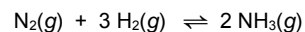
(2) Under standard conditions, $Q = 1$ and so ...

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log 1$$

(3) The Nernst equation can be applied to the overall reaction or to half-reactions individually.

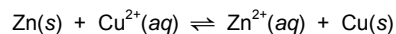
The Thermodynamic Reaction Quotient

For a gas-phase reaction, the thermodynamic reaction quotient Q is identical to Q_p .



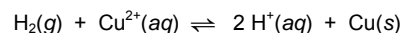
$$Q = Q_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

For a reaction that occurs in aqueous solution, Q is identical to Q_c .



$$Q = Q_c = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Q is different from Q_p or Q_c when the reaction involves gases and aqueous solutions:

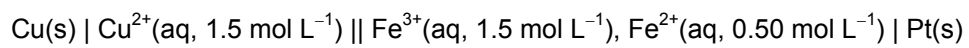


$$Q = \frac{[\text{H}^+]^2}{[\text{Cu}^{2+}] P_{\text{H}_2}}$$

Example: What is E for the half-reaction $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$

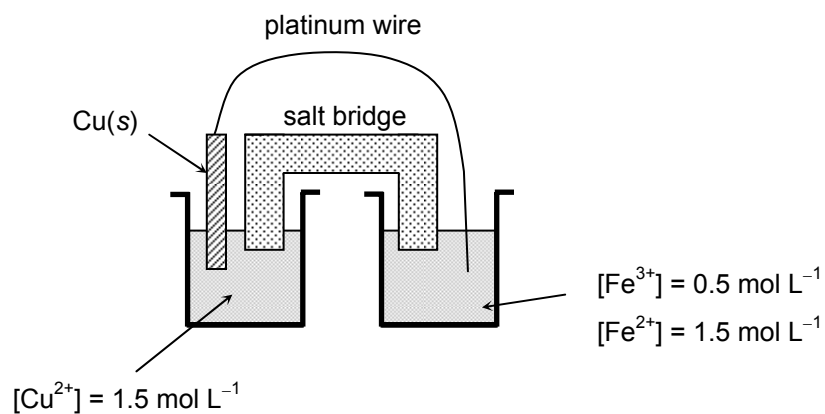
if $[\text{H}^+] = 0.10 \text{ mol L}^{-1}$ and $P_{\text{H}_2} = 1.5 \text{ atm}$?

Example: Calculate E_{cell} for the following galvanic cell.

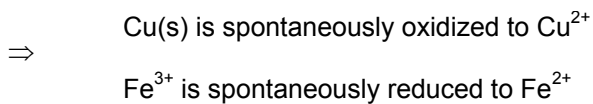


Electrochemical cells and equilibrium

In the previous example, we considered the following electrochemical cell.



We calculated that $E_{\text{cell}} = 0.454 \text{ V}$ and predicted that electrons would flow spontaneously from the copper electrode towards the $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution.

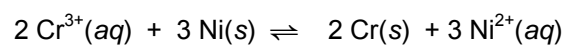


How does the reaction in the cell affect the values of Q and E_{cell} ?

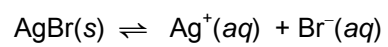
Should we expect E_{cell} to decrease indefinitely? No! We know that a closed system proceeds spontaneously towards a state of dynamic equilibrium. When equilibrium is reached, there is no further conversion of reactants into products. When an electron transfer reaction “stops”, there is no current flowing and the voltage must be zero!

At equilibrium:

Example: Use standard reduction potentials to calculate the equilibrium constant for the reaction below.

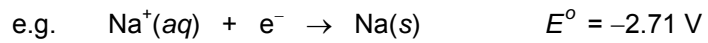


Example: Use standard reduction potentials to calculate the equilibrium constant for the reaction below.



Electrolytic cells and electrolysis

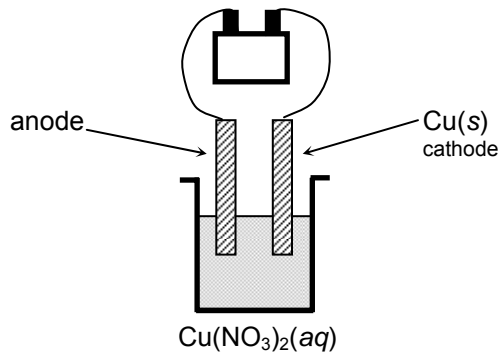
Electrolytic cells use an external voltage source to force a non-spontaneous redox reaction to occur. Electrolytic cells are useful for converting oxidized metals back into metallic form.



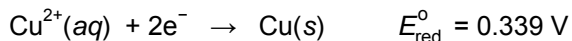
In order to reduce produce $\text{Na}(\text{s})$ from $\text{Na}^+(\text{aq})$, we would have to use an external power source capable of supplying at least 2.71 volts.

Example: A copper sulfate solution, $\text{CuSO}_4(aq)$, is electrolyzed for 7.00 minutes using an external current of 0.60 amperes. What mass of $\text{Cu}(s)$ is produced? (Note: 1 ampere = 1 coulomb per second)

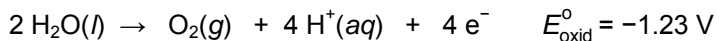
Recall: $1 \text{ mol } e^- \equiv 96\,485 \text{ C}$



The cathode reaction is:



The battery draws electrons away from the anode. If the anode is chosen to be an inert material (e.g. Pt), then what reaction is supplying these electrons? The oxidation of water!!



Without the battery, $E_{\text{cell}}^{\circ} = -0.891 \text{ V}$. In order for Cu^{2+} to be reduced, we need a battery with a voltage significantly greater than 0.891 V.