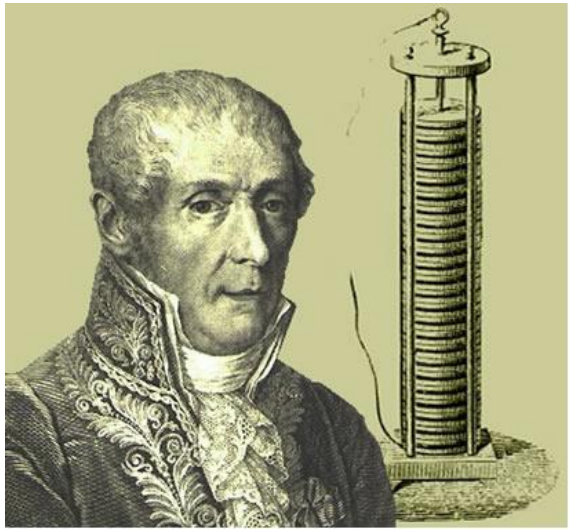
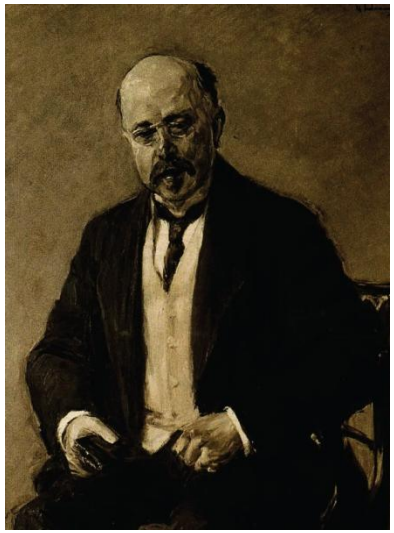
Electrochemistry

Michael Morse

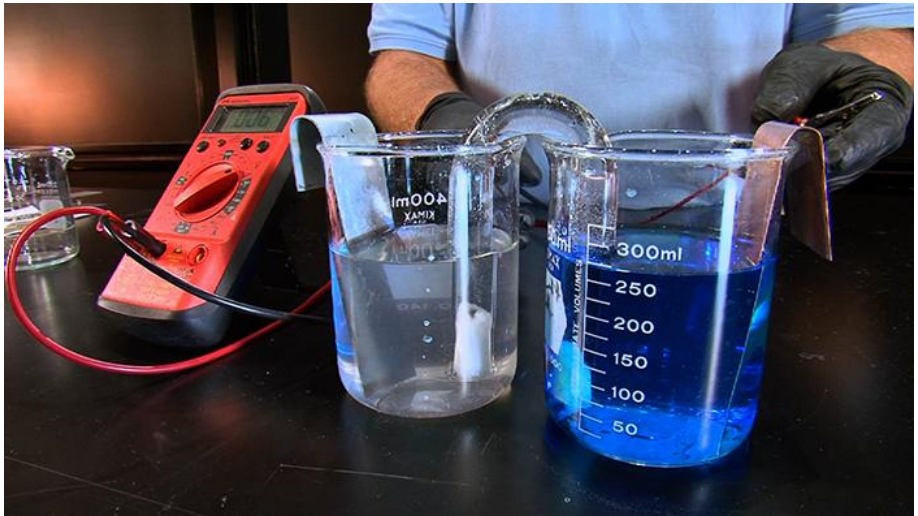


Alessandro Volta

Michael Faraday



Walther Nerst



Electrochemistry

Using electrical potentials and currents as a way to affect chemistry

Using chemistry to generate electrical potentials and currents

Using electrical potentials and currents as a way to study chemical phenomena

In all of these uses, the key is to control or use oxidation-reduction chemistry by either supplying the electrons through wires, or getting the chemistry to deliver the electrons through wires.

Oxidation-Reduction Reactions (or REDOX reactions)

The starting point for all of electrochemistry is the idea of oxidation-reduction reactions.

One reactant loses electrons (is oxidized), for example:

$$Zn \rightarrow Zn^{2+} + 2e^-$$

The other reactant gains electrons (is reduced), for example:

$$Ag^+ + e^- \rightarrow Ag$$

Here, Ag^+ causes Zn to be oxidized, so it is the oxidizing agent.

Zn causes Ag^+ to be reduced, so it is the reducing agent.

The key to electrochemistry is separating the two reactions so that they can be driven by supplying or removing electrons at an electrode. Alternatively, by forcing the electrons to run through a circuit, chemical energy can be converted into electrical energy, which can be used to perform work (a battery).

Balancing REDOX reactions

The key thing is to write the two half-reactions so that the number of electrons that move is the same for both of them. In this example, it is trivial.

$Zn \rightarrow Zn^{2+} + 2e^-$ Two electrons move

$Ag^+ + e^- \rightarrow Ag$ One electron moves

Obviously, the second half-reaction must be multiplied by 2:

$Zn \rightarrow Zn^{2+} + 2e^-$ Two electrons move

$2Ag^+ + 2e^- \rightarrow 2Ag$ Two electron moves

Add the two equations, deleting species that appear as reactants and products (the 2 electrons here), and we get a balanced reaction.

$$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$$

These can get a lot more complicated, especially for reactions that occur in acidic or basic solutions.

First a bit about oxidation numbers:

Oxidation numbers are a way of assigning electrons to atoms, but they're really just a bookkeeping device. In HI, how can the shared electrons in the H-I covalent bond be distributed so that I has both of them and H has none? Still we always assign the oxidation numbers as H^{+1} I^{-1} in this compound.

Rules:

1. In any pure element, the oxidation number is 0.
2. The oxidation number of a monatomic ion is the charge of the ion.
3. The sum of all the oxidation numbers in a polyatomic ion or molecule is the net charge (0 if it is a neutral molecule).
4. In a compound, the oxidation number of an alkali metal is always +1; alkaline earths are always +2.
5. In a compound, fluorine is always -1; Cl, Br, and I are -1 unless in compounds with oxygen or fluorine.
6. The oxidation number of oxygen in a compound is -2, unless it is combined with fluorine or is a peroxide (in which case it is -1).
7. The oxidation number of hydrogen is +1, unless it is combined with a metal, in which case it is -1.

Balancing REDOX reactions in acidic media

1. First decide what is oxidized and reduced, then write balanced half-reactions.
2. Next, multiply the half-reactions by factors so the number of electrons lost equals the number gained, and combine the two half-reactions. Delete species that are replicated on both sides.
3. Next, determine which side has more oxygen atoms, and add water molecules to the other side so that the oxygen atoms are balanced.
4. Finally, determine which side has more hydrogen atoms, and add H^+ ions to the other side so the hydrogens are balanced.
5. Check to make sure the number of atoms of each element, and the net charge on each side balances, and you're done.

Example: A REDOX reaction in acidic media

$$Cu(s) + HNO_3(aq) \rightarrow Cu(NO_3)_2\,(aq) + NO(g)$$

Oxidation #s: 0 +1 +5 -2 +2 +5 -2 +2 -2

Cu is oxidized: $Cu(s) \rightarrow Cu^{2+}\,(aq) + 2e^-$

N is reduced: $HNO_3(aq) + 3H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$

Multiply by 3 and 2, respectively, so $6e^-$ are exchanged:

$$3Cu(s) \rightarrow 3Cu^{2+}\,(aq) + 6e^-$$

$$2HNO_3(aq) + 6H^+(aq) + 6e^- \rightarrow 2NO(g) + 4H_2O(l)$$

Add the half-reactions and delete replicated species (like $6e^-$):

$$3Cu(s) + 2HNO_3(aq) + 6H^+(aq) \rightarrow 3Cu^{2+}\,(aq) + 2NO(g) + 4H_2O(l)$$

This is already balanced, because I used the rules to balance the reduction half-reaction already.

Balancing REDOX reactions in basic media

1. First decide what is oxidized and reduced, then write balanced half-reactions.
2. Next, multiply the half-reactions by factors so the number of electrons lost equals the number gained, and combine the two half-reactions. Delete species that are replicated on both sides.
3. Next, determine which side has more oxygen atoms, and add $2OH^-$ per needed O atom to the side that needs O atoms, and add one H_2O per needed O atom to the side that has excess O atoms.
4. Check to make sure the number of atoms of each element, and the net charge on each side balances, and you're done.

Example: A REDOX reaction in basic media

$$ClO^-(aq) + I^-(aq) \rightarrow IO_3^-(aq) + Cl^-(aq)$$

Oxidation #s: +1 -2 -1 +5 -2 -1

I is oxidized: $I^-(aq) \rightarrow IO_3^-(aq) + 6e^-$

Cl is reduced: $ClO^-(aq) + 2e^- \rightarrow Cl^-(aq)$

We can balance these half-reactions with regard to O and H atoms first or later. This time, I'll balance them later.

Multiply the second reaction by 3, so $6e^-$ are exchanged:

$$I^-(aq) \rightarrow IO_3^-(aq) + 6e^-$$

$$3ClO^-(aq) + 6e^- \rightarrow 3Cl^-(aq)$$

Add these equations and delete replicated species (like $6e^-$):

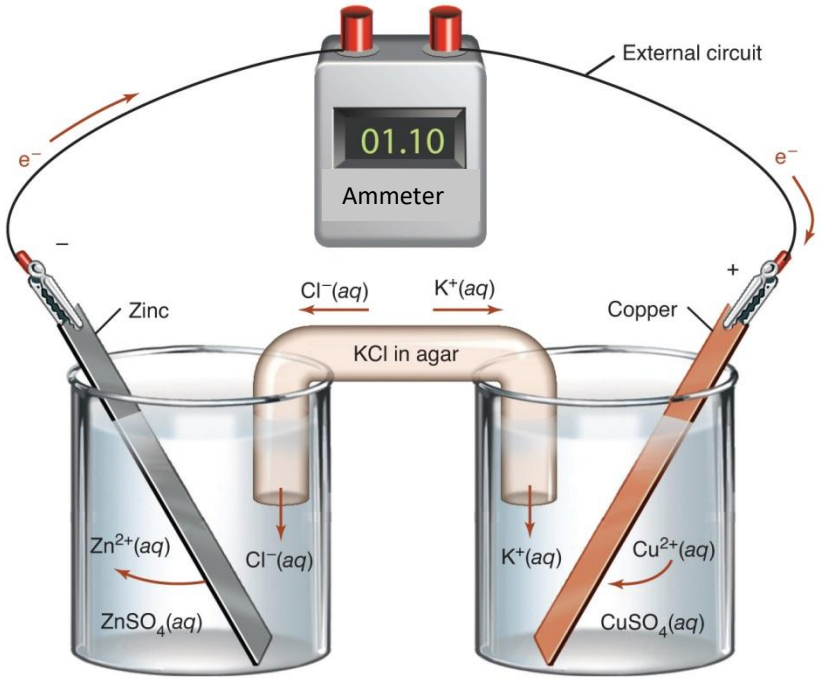
$$I^-(aq) + 3ClO^-(aq) \rightarrow IO_3^-(aq) + 3Cl^-(aq)$$

It's already balanced! No need to add OH^- or water.

Equivalently, I could have balanced each half-reaction first by addition OH^- and H_2O. For example, the I oxidation reaction has an excess of 3 O atoms on the right, so I need to add 6 OH^- ions on the left and 3 H_2O molecules on the right, to give:

$$6OH^- + I^-(aq) \rightarrow IO_3^-(aq) + 6e^- + 3H_2O(l)$$ BALANCED!!

Faraday's Law of Electrolysis



$$n = \frac{Q}{zF}$$

The number of moles of a substance produced or consumed at an electrode (n) equals the total charge that has flowed through the system (Q, in Coulombs), divided by the valency number of the ion (z, an integer) times a constant, F.

F is now called the Faraday constant:
F= 96,485 C/mol.

In this example, the number of moles of copper that are deposited on the copper electrode would be given by Q/2F because 2 electrons are required to reduce Cu^{2+} to Cu.

Now we would recognize z as the number of electrons transferred in order to cause the oxidation or reduction.

Question: At a current of 1 Ampere (1 Coulomb/sec), how long does it take to deposit 1 g of Cu onto a surface?

Faraday's Law of Electrolysis

Question: At a current of 1 Ampere (1 Coulomb/sec), how long does it take to deposit 1 g of Cu onto a surface?

Solution:

First convert 1 g to moles: n= 1 g/(63.55 g/mol) = 0.01574 mol

Next, Q = 1 Ampere × t because Coulombs = Amperes × time (s).

z=2 because 2 electrons are required to reduce Cu^{2+}(aq) to Cu(s).

Now, using $n = \frac{Q}{zF}$ we get

0.01574 mol = [(1 C/s) × t]/ (2 × 96,485 C/mol)

$$0.01574\ mol = \frac{\left(1\frac{C}{s}\right)t}{2 \times 96{,}485\ C/mol}$$

$$0.01574\ mol = \frac{\left(1\frac{C}{s}\right)t \cdot mol}{2 \times 96{,}485\ C}$$

Solving for t:

$$t = (0.01574\ mol) \times (2\ \times 96{,}485\ C/mol) \times \left(\frac{s}{1C}\right) = 3{,}036\ s \text{ or } 50.6 \text{ minutes}$$

Follow-up question:

Kennecott produces 300,000 tons of copper/year. How many Coulombs of electrons do they require per year? [Answer: 8.3×10^{14} Coulombs or 5.16×10^{33} electrons.]

Current *vs*. Voltage

Faraday's Law – the total charge (or current integrated over time) governs how much material is oxidized or reduced.

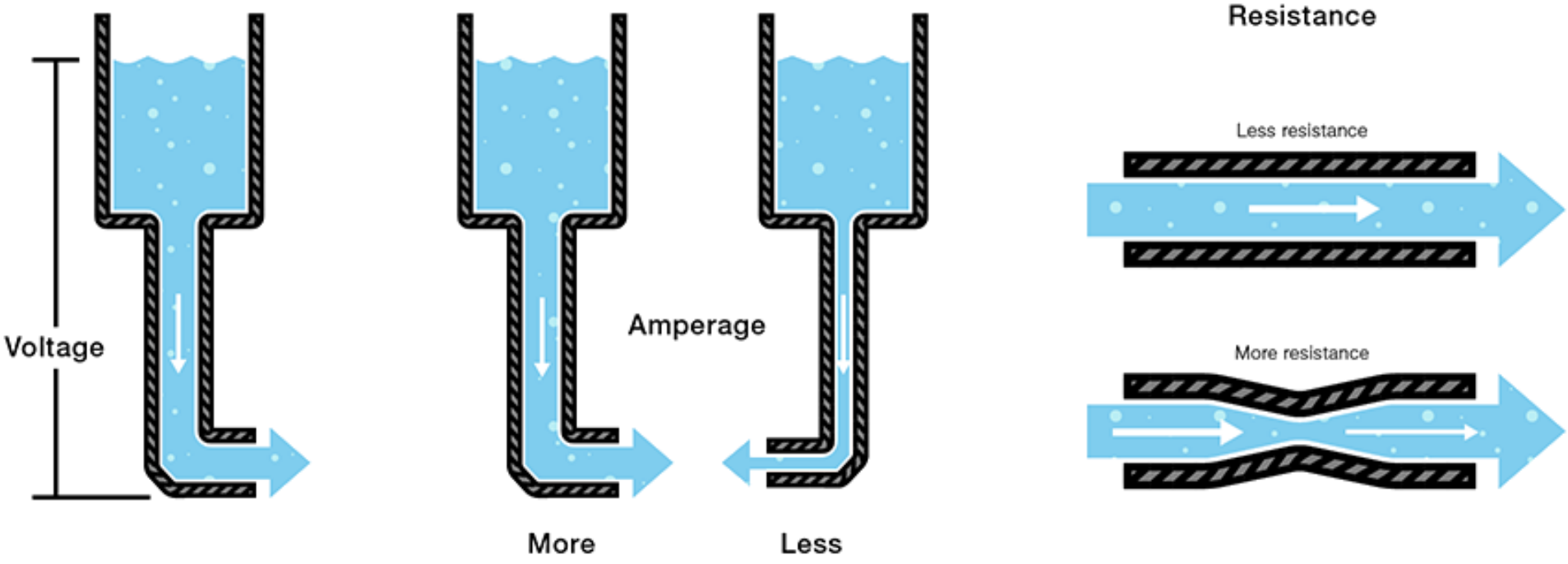
For galvanic or voltaic cells, we're concerned with *voltage*.

How can you understand the difference between current and voltage?

Current is easy – how many electrons pass a given point per second.

Voltage is related to the driving force that pushes the electrons to their destination. In electrochemistry, it is sometimes called the electromotive force (emf), measured in volts.

Current *vs*. Voltage

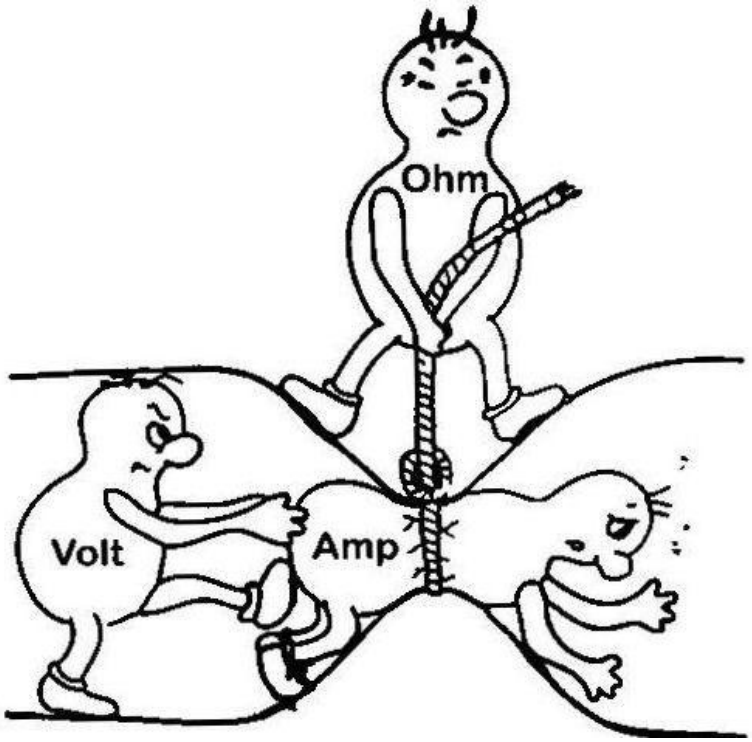


In fluid flow, the driving force is the pressure difference between the source and the sink.
In electricity, the driving force is the voltage difference between the electron source and sink.

In fluid flow, the current is how many liters of fluid flow past a point per second (L/s).
In electricity, the current is how many electrons flow past a point per second (C/s).

In both cases, there is resistance to flow, which slows the flow, takes some of the potential energy, and releases it as heat.

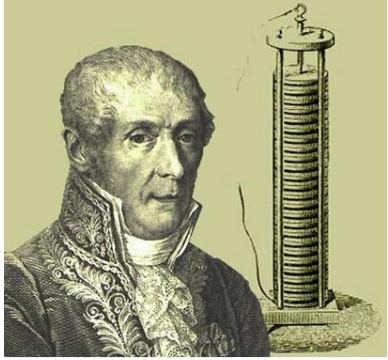
Current *vs*. Voltage



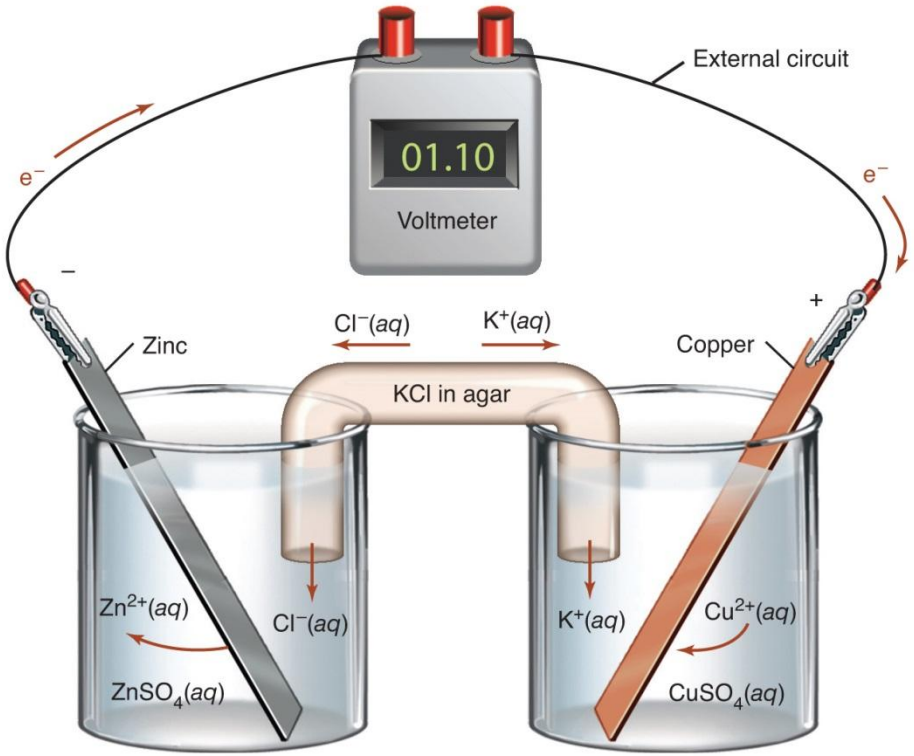
Potential Difference (V, volts) = Current (I, amps) × Resistance (R, ohms)

For a given potential difference, to increase current, you must decrease the resistance.

Galvanic or Voltaic Cells



A galvanic cell is a redox reaction, where the chemicals are separated in order to force the electrons to go through wires so they can do work.



Here, the two half-reactions:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (wire)

and

$Cu^{2+}(aq) + 2e^-$ (wire) $\rightarrow Cu(s)$

supply a driving force of 1.10 V.

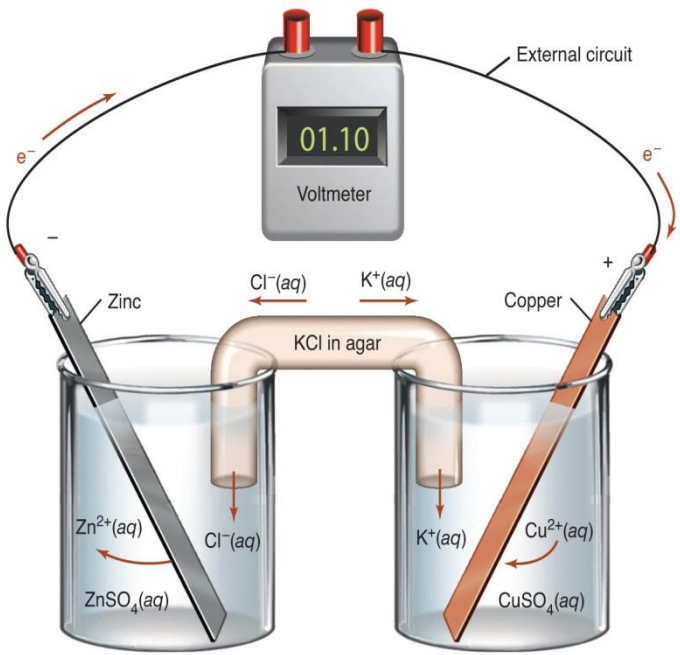
Cu^{2+} is removed from the right-hand beaker, so positive charge must be replenished.

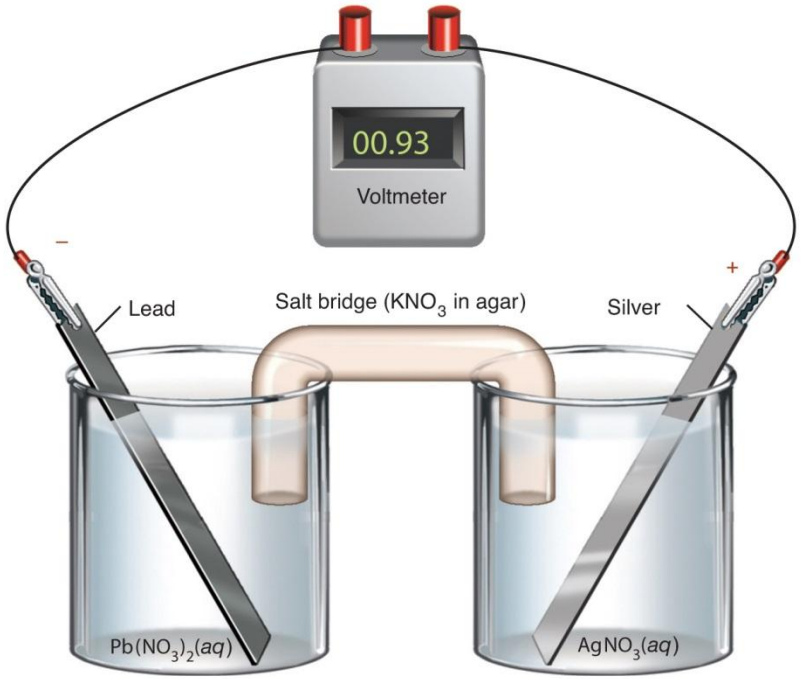
Zn^{2+} is added to the left-hand beaker, so negative charge must be added to it.

This is done by the KCl salt bridge. Otherwise, the cell shuts down.

Galvanic or Voltaic Cells

Different metals produce different voltages:





$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (wire)

$Cu^{2+}(aq) + 2e^-$ (wire) $\rightarrow Cu(s)$

gives 1.10 V

$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$ (wire)

$Ag^+(aq) + e^-$ (wire) $\rightarrow Ag(s)$

gives 0.93 V

Standard Reduction Potentials

Experiments show that the voltages produced by various pairs of metals are related:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (wire)
$Cu^{2+}(aq) + 2e^-$ (wire) $\rightarrow Cu(s)$ gives 1.10 V

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (wire)
$Ag^+(aq) + e^-$ (wire) $\rightarrow Ag(s)$ gives 1.56 V

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ (wire)
$Ag^+(aq) + e^-$ (wire) $\rightarrow Ag(s)$ gives 0.46 V

This fits into a nice pattern if each half-reaction is assigned a standard reduction potential, $\mathcal{E}^0$:

Half-reaction	$\mathcal{E}^0$	Cell	Voltage
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.337 V	Ag/Cu	0.800 V - 0.337 V = 0.463 V
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.800 V	Ag/Zn	0.800 V –(-0.762 V) = 1.562V
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.762 V	Cu/Zn	0.337 V – (-0.762 V) = 1.099 V

The voltage produced is just the standard reduction potential of the substance that is reduced minus the reduction potential of the substance being oxidized.

Standard Reduction Potentials

Signs matter! So it is good to have some conventions.

It turns out that $\mathcal{E}^0$ is related to thermodynamics (namely ΔG), so if we consider the actual reaction, we can combine the $\mathcal{E}^0$ values for the two half-reactions by writing them in opposite senses:

From the table of $\mathcal{E}^0$ values:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ 0.337 V

$Ag^+(aq) + e^- \rightarrow Ag(s)$ 0.800 V

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ -0.762 V

If we consider the cell

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\mathcal{E}^0$ = +0.762 V (reversed because we've reversed the reaction)

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\mathcal{E}^0$ = 0.337 V

Total voltage produced is the sum of that for the two half-reactions, 1.099 V

These two half-reactions produce a positive voltage difference, and the reactions do occur spontaneously in this direction, giving a negative ΔG.

Connection to ΔG

The free energy is the energy in a system that is available to do work.
For a system at constant pressure, the appropriate free energy is G, the Gibbs free energy, so we have:

-ΔG = work that can be done by the system

If a charge (q, in Coulombs) is moved from a potential V_1 to V_2 (in volts), work is done on the charge in the amount $q\Delta V = q\,\mathcal{E}$.

So, we get

$-\Delta G = q\,\mathcal{E}$ (q is in Coulombs)
or
$-\Delta G = nF\,\mathcal{E}$ (n is the number of moles of electrons moved, F= 96,485 C/mol)
For example, for our electrochemical system: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
we had a net $\mathcal{E}^0$ = 1.099 V
so $\Delta G° = -nF\mathcal{E}^0$ = -(2 moles)(96,485 C/mol)(1.099 V) = -212,074 CV
But 1 Coulomb × 1 Volt = 1 Joule, so ΔG°=- 212,074 J = -212 kJ
The reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$ has ΔG°= -212 kJ/mol

Connection to ΔG

Electrochemistry can be used to determine equilibrium constants that are far beyond the range of direct measurement:

For $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$, we've determined that $\Delta G° = -212$ kJ/mol.

But we know that $\Delta G° = -RT\ lnK$

So, using $K = e^{-\frac{\Delta G°}{RT}}$ we get:

$K = \exp((212{,}000\ J/mol)/(8.314\ J/(mol\text{-}K) \times 298K)) = \exp(85.6) = 1.45 \times 10^{37}$

Good luck finding any Cu^{2+} ions in a beaker that contains a strip of zinc that has reached equilibrium!

The Nerst Equation

The tables of standard reduction potentials are listed based on the reactants and products being in the standard states (1 M concentrations). What if they aren't?
We know how ΔG depends on concentration:

$$\Delta G = \Delta G° + RT\ ln\frac{([C])^c([D])^d}{([A])^a([B])^b}$$

Here, [C] and [D] are concentrations of products, [A] and [B] are concentrations of reactants
Because -ΔG = nF $\mathcal{E}$, this gives

$$\frac{\Delta G}{nF} = \frac{\Delta G°}{nF} + \frac{RT}{nF}\ ln\frac{([C])^c([D])^d}{([A])^a([B])^b}$$

or

$$-\frac{\Delta G}{nF} = -\frac{\Delta G°}{nF} - \frac{RT}{nF}\ ln\frac{([C])^c([D])^d}{([A])^a([B])^b}$$

or

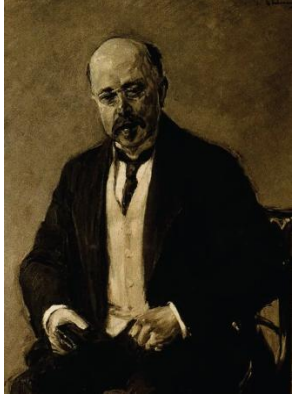
$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{nF}\ ln\frac{([C])^c([D])^d}{([A])^a([B])^b}$$

At T = 298.15K = 25.00°C, $\mathcal{E} = \mathcal{E}^0 - \frac{0.02569}{n}\ ln\frac{([C])^c([D])^d}{([A])^a([B])^b}$

$$\boxed{\mathcal{E} = \mathcal{E}^0 - \frac{0.05916}{n}\ log\frac{([C])^c([D])^d}{([A])^a([B])^b}}$$

The Nernst Equation

The Nerst Equation



The Nernst Equation

$$\mathcal{E} = \mathcal{E}^0 - \frac{0.05916}{n}\, log \frac{([C])^c([D])^d}{([A])^a([B])^b}$$

tells us how the voltage put out by a battery will change as it discharges, and the concentrations of products build up.

For example, if we start off with concentrations of 1 M Zn^{2+} and 1M Cu^{2+} in our cell:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ or $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

We get the standard $\mathcal{E}^0$ = 1.099 V.

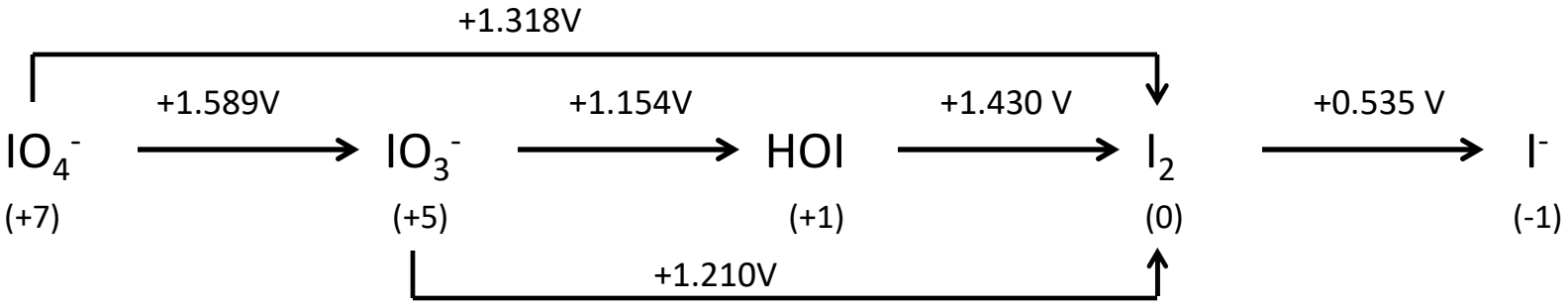
When the cell has been half discharged, $[Cu^{2+}]$ = 0.5M. If the volume for the Zn^{2+} ions is the same as that for the Cu^{2+} ions, then $[Zn^{2+}]$ = 1.5M, and the cell will now generate a voltage difference of:

$$\mathcal{E} = 1.099V - \frac{0.05916}{2}\, log \frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.099V - \frac{0.05916}{2}\, log \frac{1.5M}{0.5M} = \boxed{1.085\ \text{V}}$$

What will the cell generate when it is 90% or 99% discharged?

A Conundrum

A Latimer diagram relates a series of oxidation states of an element:

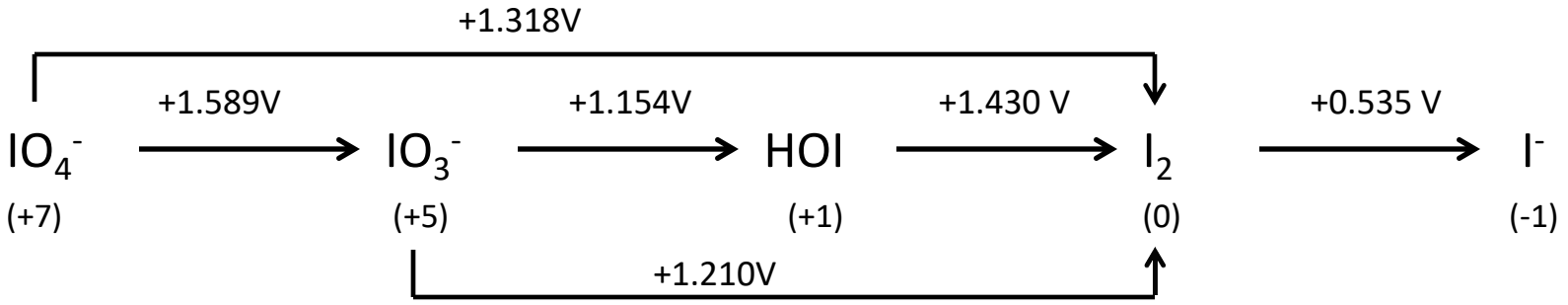


Why doesn't the $\mathcal{E}^0$ value for $IO_4^- \rightarrow I_2$ equal 1.589 V + 1.154 V + 1.430 V = 4.173 V ?

The actual value is only 1.318 V!

$\mathcal{E}^0$ Values Are Not Additive! (but ΔG values are)

A Latimer diagram relates a series of oxidation states of an element:



Using $\Delta G = -nF\mathcal{E}$, the IO_4^- ⟶ I_2 reaction can be broken into 3 steps:

$\Delta G_1 = -2F(1.589V)$

$\Delta G_2 = -4F(1.154V)$

$\Delta G_3 = -1F(1.430V)$

$\Delta G_{total} = -2F(1.589V) - 4F(1.154V) - 1F(1.430V) = -nF\mathcal{E}_{total} = -7F\mathcal{E}_{total}$

$\therefore \mathcal{E}_{total} = [2(1.589V) + 4(1.154V) + 1(1.430V)]/7$

$$\mathcal{E}_{total} = \frac{2}{7}(1.589\ V) + \frac{4}{7}(1.154\ V) + \frac{1}{7}(1.430\ V) = 1.318\ V$$

The reduction potential for a multi-step process is just the weighted average of the potentials for each step, where the weighting factor is the number of electrons transferred in that step.

Why are some oxidation agents so much more effective in acidic solution than basic solution?

Example:

$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-$ $\qquad \mathcal{E}^0 = +0.60\ V$

$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2(s) + 2H_2O$ $\qquad \mathcal{E}^0 = +1.70\ V$

Why is permanganate such a powerful oxidation agent in acidic media, but much less powerful in basic conditions?

Can these two values of $\mathcal{E}^0$ be related?

The importance of pH

These are really just the same reaction, run at two different pH values!

MnO_4^- + $2H_2O$ + $3e^-$ ⟶ $MnO_2(s)$ + $4OH^-$ $\quad \mathcal{E}^0 = +0.60\ V$

MnO_4^- + $4H^+$ + $3e^-$ ⟶ $MnO_2(s)$ + $2H_2O$ $\quad \mathcal{E}^0 = +1.70\ V$

Remember: the standard reduction potential assumes all concentrations are 1 M.

If we run the first reaction at pH 1, $[OH^-] = 10^{-14}$M, and we use the Nerst equation to find the $\mathcal{E}$ for this condition.

The Nernst equation: $$\mathcal{E} = \mathcal{E}^0 - \frac{0.05916}{n}\ log\ \frac{([C])^c([D])^d}{([A])^a([B])^b}$$

For this example: $$\mathcal{E} = \mathcal{E}^0 - \frac{0.05916}{3}\ log\ \frac{([OH^-])^4}{([MnO_4^-])^1}$$

Plugging in the specifics: $$\mathcal{E} = \mathcal{E}^0 - \frac{0.05916}{3}\ log\ \frac{([10^{-14}])^4}{([1])^1}$$

$$\mathcal{E} = +0.60 - \frac{0.05916}{3}\big(4(-14) - 1(0)\big) = 1.70\ V$$

Under acidic conditions (pH = 1, $[H^+]$ = 1M), we get $\mathcal{E}^0$ = 1.70 V, just as the table says.

Thanks for your attention!