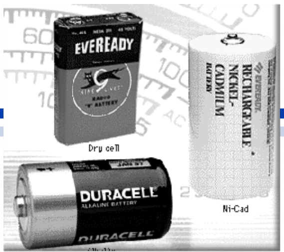
Electrochemistry

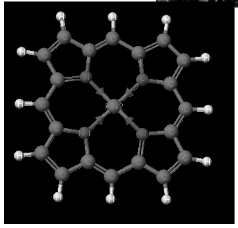
CHEM 102
T. Hughbanks

Electrochemistry



Applications:

- Batteries
- Corrosion
- Industrial production of chemicals such as Cl_2, NaOH, F_2 and Al
- Biological electron transfer reactions



The heme group

Preliminary Concepts

- Electrochemistry: the electrical generation of, or electrical exploitation of oxidation reduction reactions.
- Electrochemical reactions involve some means of producing or consuming electrons from an external source. The reacting system is an electrochemical cell and the electrical current enters or exits via electrodes.

More Preliminary Concepts

- Electrodes:

  Reduction occurs at one electrode (Cathode)

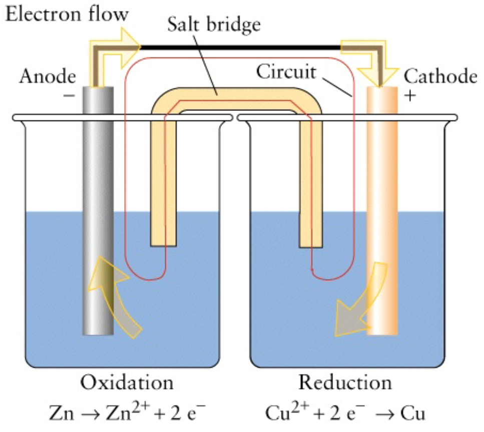
  Oxidation occurs at the other electrode (Anode)
- Electrical Conduction: movement of electrical charges from one place to another - usually through some medium. If the medium is a wire, it is metallic conduction; if the medium is an electrolyte solution, the conduction is carried out by ions.

Electrochemical Cells

There are two kinds:

- Electrolytic: electrical current is used to drive otherwise nonspontaneous oxidation-reduction (redox) reactions
- Galvanic (Voltaic): Spontaneous redox reactions are used to create electrical current (and do electrical work).

Daniell Cell



$Zn|Zn^{2+}(1.0M)||Cu^{2+}(1.0M)|Cu$

“Separation” in a Galvanic cell:

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

Cathode reaction:

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

Anode reaction:

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

Note: Despite what the picture seems to imply, electrons don’t carry the current in solution!

Cell Notation

Phase boundary Salt Bridge Phase boundary

$\mathrm{Zn|Zn^{2+}(1.0M)||Cu^{2+}(1.0M)|Cu}$

Anode Information Cathode Information

Phase boundaries Salt Bridge Phase boundary

$\mathrm{Pt|H_2(1\ bar)|H^{+}(1.0M)\ ||Cu^{2+}(1.0M)|Cu}$

Anode Information Cathode Information

Terminology for Redox Reactions

- OXIDATION: loss of electron(s) by a species; increase in oxidation number.
- REDUCTION: gain of electron(s); decrease in oxidation number.
- OXIDIZING AGENT: electron acceptor; species is reduced.
- REDUCING AGENT: electron donor; species is oxidized.

Simple (innocent) Redox Reactions

The simplest Oxidation-Reduction (Redox) reactions are those wherein only electrons are transferred, eg.:

$$Co^{3+}(aq) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe^{3+}(aq)$$

$$Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

In these reactions, $Fe^{2+}(aq)$ is the *reducing agent* (*reductant*); $Co^{3+}(aq)$ and $Ce^{4+}(aq)$ are *oxidizing agents* (*oxidants*).

$Fe^{2+}(aq)$ is oxidized (its oxidation state increases)

$Co^{3+}(aq)$ and $Ce^{4+}(aq)$ are reduced (their oxidation states decrease).

More on Redox Reactions

In the previous reactions, the uninvolved ions are not shown, but if they are it doesn't really change what is actually going on. e.g. in aqueous solution, the reaction

$$Co(NO_3)_3 + Fe(NO_3)_2 \rightarrow Co(NO_3)_2 + Fe(NO_3)_3$$

involves transfer of electrons among the metal ions.

Slightly more complicated are reactions involving bond breaking or making, e.g.,

$$2\ Cu^{+}(aq) + I_2(s) \rightarrow 2\ Cu^{2+}(aq) + 2\ I^{-}(aq)$$

$Cu^{+}(aq)$ is oxidized to Cu^{2+} (its *oxidation state increases*).

I_2 is reduced to I^{-} (*oxidation state decreases – it's reduced*).

More on Redox Reactions

Sometimes a redox reaction can involve fairly extensive structural rearrangement and atom transfer among the molecules involved:

$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$ - not balanced

This shows the species that are oxidized and reduced, but doesn’t indicate all the chemical species involved. This occurs in acidic solution, so we can assume that “protons” are involved with the oxygen atoms lost by the dichromate ions - and we must take account of the number of electrons transferred:

$14\ H^+ + Cr_2O_7^{2-}(aq) + 6\ Fe^{2+}(aq) \rightarrow 2\ Cr^{3+}(aq) + 6\ Fe^{3+}(aq) + 7\ H_2O$

Things that must check: (1) atoms, (2) charge, (3) species shown “make sense” for an acidic solution

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Half Reactions

$$Co^{3+}(aq) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe^{3+}(aq)$$

Half-reactions:

$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	reduction reaction (Cathode reaction)
$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$	oxidation reaction (Anode reaction)

Even though the electrons are never really “free” we can break up the redox process into half reactions for the purpose of “bookkeeping” in balancing equations.

If you like mnemonics…

Dr. Schaefer's favorites

◆ *Red Cat* - **Red**uction occurs at the **Cat**hode

◆ *An Ox* – the **An**ode is **Ox**idized

I prefer

◆ *Cations go to* the **Cat**hode (and get reduced)

◆ *Anions go to* the **An**ode (and get oxidized)

Balancing Redox Equations

Step 1: Divide the reaction into half-reactions, one for oxidation and the other for reduction.

Ox $\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)}$

Red $\mathrm{Ag^{+}(aq)} \rightarrow \mathrm{Ag(s)}$

Step 2: Balance each for mass. Already done in this case.

Step 3: Balance each half-reaction for charge by adding electrons.

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

Red $\mathrm{Ag^{+}(aq)} + e^{-} \rightarrow \mathrm{Ag(s)}$

Balancing Redox Equations

Step 4: Multiply each half-reaction by a factor so that the reducing agent supplies as many electrons as the oxidizing agent requires.

Reducing agent: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Oxidizing agent: $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

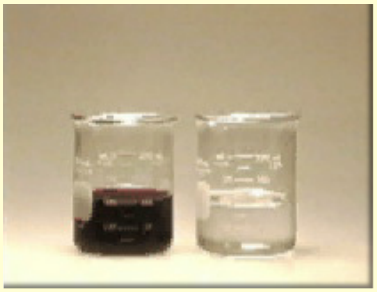
Step 5: Add half-reactions to give the overall equation.

$$Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

The equation is now balanced for both charge and mass.

Balancing Redox Equations

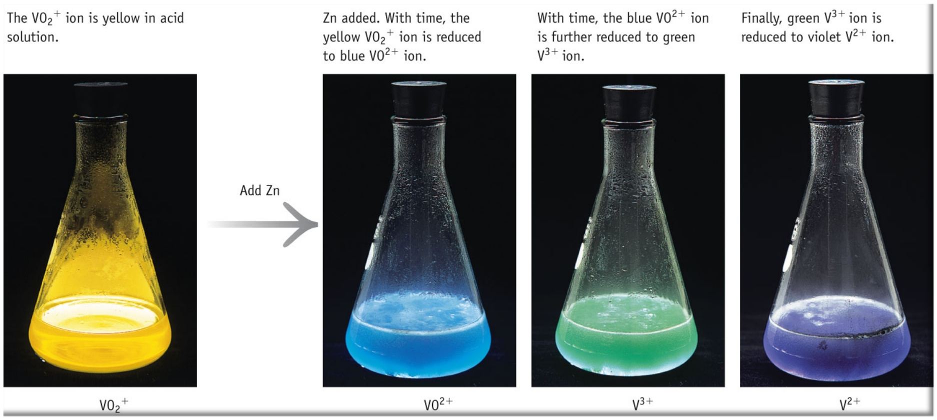
Some redox reactions have equations that must be balanced by special techniques



$$MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \rightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$$

Mn = +7 Fe = +2 Mn = +2 Fe = +3

Reduction of VO_2^+ by Zn



The VO_2^+ ion is yellow in acid solution.

Zn added. With time, the yellow VO_2^+ ion is reduced to blue VO^{2+} ion.

With time, the blue VO^{2+} ion is further reduced to green V^{3+} ion.

Finally, green V^{3+} ion is reduced to violet V^{2+} ion.

Balancing Redox Equations

Balance the following in acid solution:

$$VO_2^+ + Zn \rightarrow VO^{2+} + Zn^{2+}$$

Step 1: Write the half-reactions

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

Red $VO_2^+ \rightarrow VO^{2+}$

Step 2: Balance each half-reaction for mass.

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

Red $2\ H^+ + VO_2^+ \rightarrow VO^{2+} + H_2O$

Add H_2O on O-deficient side and add H^+ on other side for H-balance.

Balancing Redox Equations

Step 3: Balance half-reactions for charge.

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

Red $e^- + 2\,H^+ + VO_2^+ \rightarrow VO^{2+} + H_2O$

Step 4: Multiply by an appropriate factor.

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

Red $2e^- + 4\,H^+ + 2\,VO_2^+ \rightarrow 2\,VO^{2+} + 2\,H_2O$

Step 5: Add *balanced* half-reactions

$Zn + 4\,H^+ + 2\,VO_2^+ \rightarrow Zn^{2+} + 2\,VO^{2+} + 2\,H_2O$

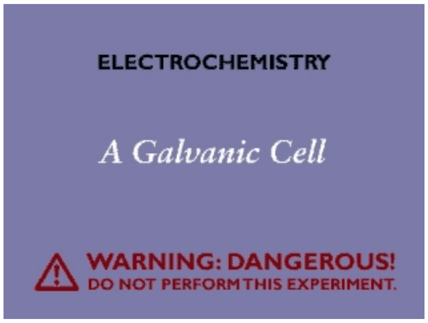
Tips on Balancing Redox Equations

- Never add O_2, O atoms, or O^{2-} to balance oxygen.
- Never add H_2 or H atoms to balance hydrogen.
- Be sure to write the correct charges on all the ions.
- Check your work at the end to make sure mass and charge are balanced.
- PRACTICE!

Examples (Unbalanced)

1. $\mathrm{MnO_4^-}(aq) + \mathrm{H^+}(aq) + \mathrm{Cl^-}(aq) \rightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{H_2O} + \mathrm{Cl_2}(g)$
2. $\mathrm{F_2}(g) + \mathrm{H_2O}(l) \rightarrow \mathrm{HF}(aq) + \mathrm{O_2}(g)$
3. $\mathrm{Ca_3(PO_4)_3}(s) + \mathrm{SiO_2}(g) + \mathrm{C}(s) \rightarrow \mathrm{P_4}(g) + \mathrm{CaSiO_3}(s) + \mathrm{CO}(g)$
4. $\mathrm{InCl}(s) + xs\ \mathrm{H_2O}(l) \rightarrow \mathrm{In}(s) + \mathrm{In^{3+}}(aq) + \mathrm{Cl^-}(aq)$
5. $\mathrm{BrO_3^-}(aq) + \mathrm{Br^-}(aq) + \mathrm{H^+}(aq) \rightarrow \mathrm{Br_2}(l) + \mathrm{H_2O}(l)$
6. $\mathrm{H_2S}(g) + \mathrm{SO_2}(g) \rightarrow \mathrm{S}(s) + \mathrm{H_2O}(l)$

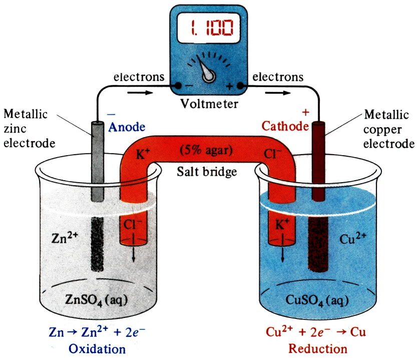
Galvanic (Voltaic) cells



ELECTROCHEMISTRY

A Galvanic Cell

⚠ WARNING: DANGEROUS!
DO NOT PERFORM THIS EXPERIMENT.



$\mathrm{Zn|Zn^{2+}(1.0M)||Cu^{2+}(1.0M)|Cu}$

The Free Energy of a redox reaction (ΔG°_{rxn}) can be harnessed by separating the oxidizing and reducing agents and forcing the electrons through a load.

Another Redox Reaction

With a strong oxidant, Cu can donate electrons:

$2\ \mathrm{AgNO_3}(aq) + \mathrm{Cu(s)} \rightarrow \mathrm{Cu(NO_3)_2}(aq) + 2\ \mathrm{Ag(s)}$

The net ionic reaction is:

$$2\ \mathrm{Ag^+}(aq) + \mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}}(aq) + 2\ \mathrm{Ag(s)}$$

Again, the reaction is really an equilibrium, but K_{eq} is huge:

$\Delta G°_{rxn} = \sum\Delta G°_{f,products} - \sum\Delta G°_{f,reactants} = -88.73\ \mathrm{kJ}$

Half Reactions

<u>Half-reactions</u>:

$\mathrm{Ag^+}(aq) + e^- \rightarrow \mathrm{Ag(s)}$ Cathode reaction

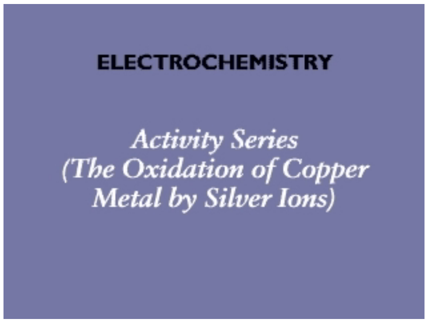
(reduction reaction)

$\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}}(aq) + 2\ e^-$ Anode reaction

(oxidation reaction)

Again, the reactions can be “separated” in a Galvanic cell.

Cu/Cu^{2+} anode, Ag/Ag^{+} cathode



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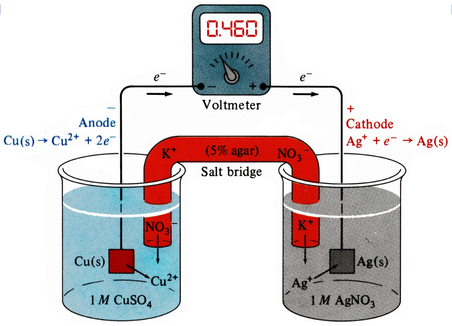
Activity Series
(The Oxidation of Copper Metal by Silver Ions)

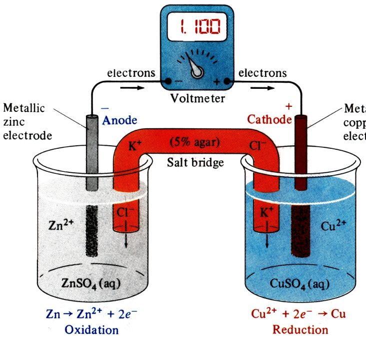


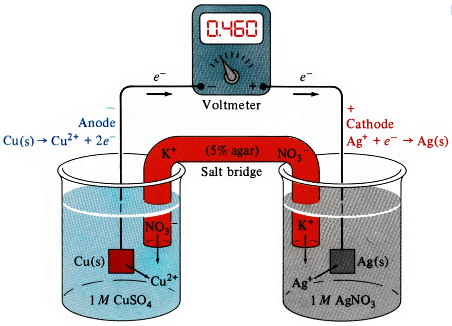
Cu|Cu^{2+}(1.0M)||Ag^{+}(1.0M)|Ag

$$2\ Ag^{+}(aq) + Cu(s) \rightarrow\ Cu^{2+}(aq) + 2\ Ag(s)$$

$$\Delta G°_{rxn} = \Sigma\Delta G°_{f,products} - \Sigma\Delta G°_{f,reactants} = -88.73\ kJ$$

Additivity of Cell Potentials





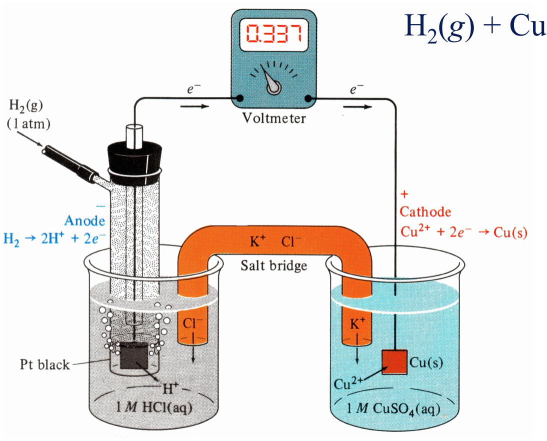
$$2\ Ag^{+}(aq) + Zn(s)\ \rightarrow\ Zn^{2+}(aq) + 2\ Ag(s)$$

$E°_{cell}$ = 1.100 V + 0.460 V = 1.56 V (wired in series)

$$\Delta G°_{rxn} = \Sigma\Delta G°_{f,products} - \Sigma\Delta G°_{f,reactants} = -301.28\ kJ$$

Standard Hydrogen Electrode, SHE

$Pt|H_2(1\ bar)|H^+(1.0M)\ ||Cu^{2+}(1.0M)|Cu$



$H_2(g) + Cu^{2+}(aq) \rightarrow 2\ H^+(aq) + Cu(s)$

$E°_{cell} = 0.337$ V

All potentials can be referenced to one standard electrode. That electrode is the Standard Hydrogen Electrode shown here.

Standard Reduction Potentials

Reduction Half-reaction	$E°$ (V)
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$2\ H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00 (by defn.)
$Zn^{2+}(aq) + 2e^- \rightarrow Zn\ (s)$	-0.76

The choice of SHE sets the zero of the scale, but all the measurable cell potentials don't depend on that choice.

From Red. Potentials to Cell Potentials

Reduction Half-reaction	*E*° (V)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	[-0.76]
$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$	1.10

The choice of SHE sets the zero of the scale, but all the measurable cell potentials don't depend on this choice.

Using the Electromotive Series -

"Recipe" for Evaluating Redox Rxns' Spontaneity

- Find the appropriate half-reactions
- Write the half-reactions with the most positive (or "least negative") value first.
- Write the other half-rxn as an oxidation and write its oxidation potential (= – reduction potential)
- Balance the half-rxns. with respect to e^- transfer. (<u>Don't multiply the potentials by the multiplicative constant used in balancing</u>.)
- Add half-rxns and *E*°'s to get $\boldsymbol{E}^{\circ}_{\mathbf{cell}}$, if > 0, it's spontaneous.