FUNDAMENTALS OF ELECTROCHEMISTRY

CHEM*7234 / CHEM 720

Lecture 1

5/7/03

Course Overview

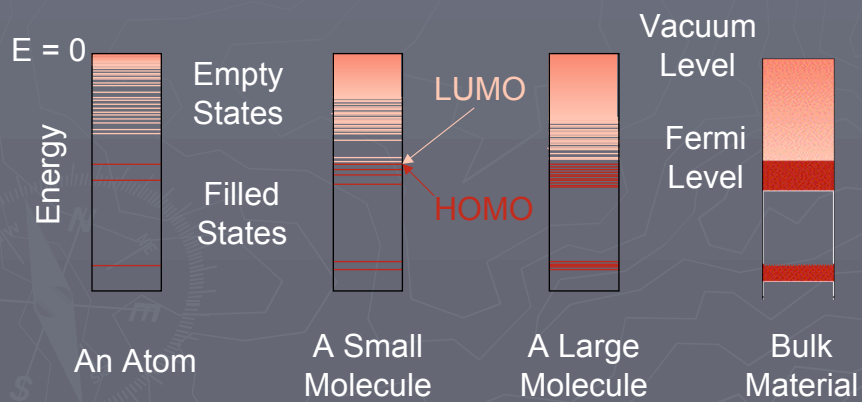| Date	Topic	Instructor
Thurs 8	Thermodynamics; Cell Potentials, Nernst equation	D. Thomas
Fri 9	The Electrode/Solution Interface	J. Lipkowski
Mon 12	Electrode Kinetics and Mass Transport	J. Lipkowski
Tues 13	Instrumentation	G. Szymanski
Wed 14	Voltammetric Methods	M. Baker
Thurs 15	Chronometric Methods	I. Burgess
Fri 16	Impedance Methods	J. Noel
Mon 19	Victoria Day Holiday	
Tues 20	Industrial Applications: Sensors	N. Bunce
Wed 21	Organic Electrochemistry	A. Houmam
Thurs 22	Industrial Applications: Hydrothermal Electrochemistry	P. Tremaine
	Industrial Applications: Fuel Cells and Batteries	D. Malevich
Fri 23	Imaging/ Surface Analytical Methods	D. Thomas

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Course Evaluation

Assignments: Five Assignments, about every other day. Each will consist of three
    questions. These assignments will count for 60% of the course grade.

Final Exam: May 30 in AXEL 259. There will be eight questions. You will choose to answer
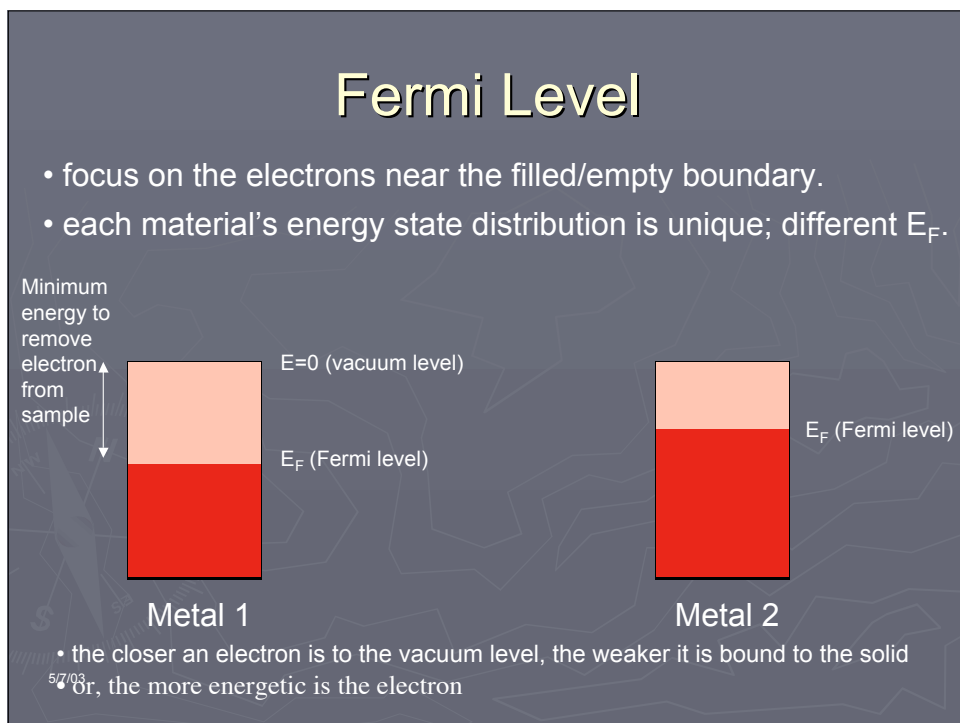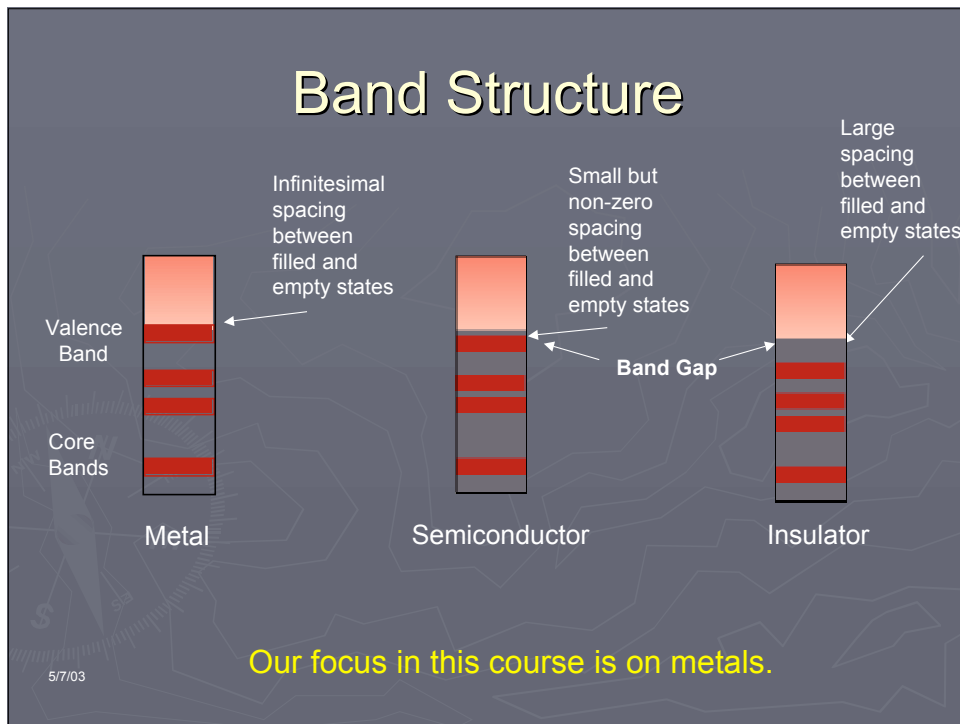   six of them. It will count for 40% of the course grade.

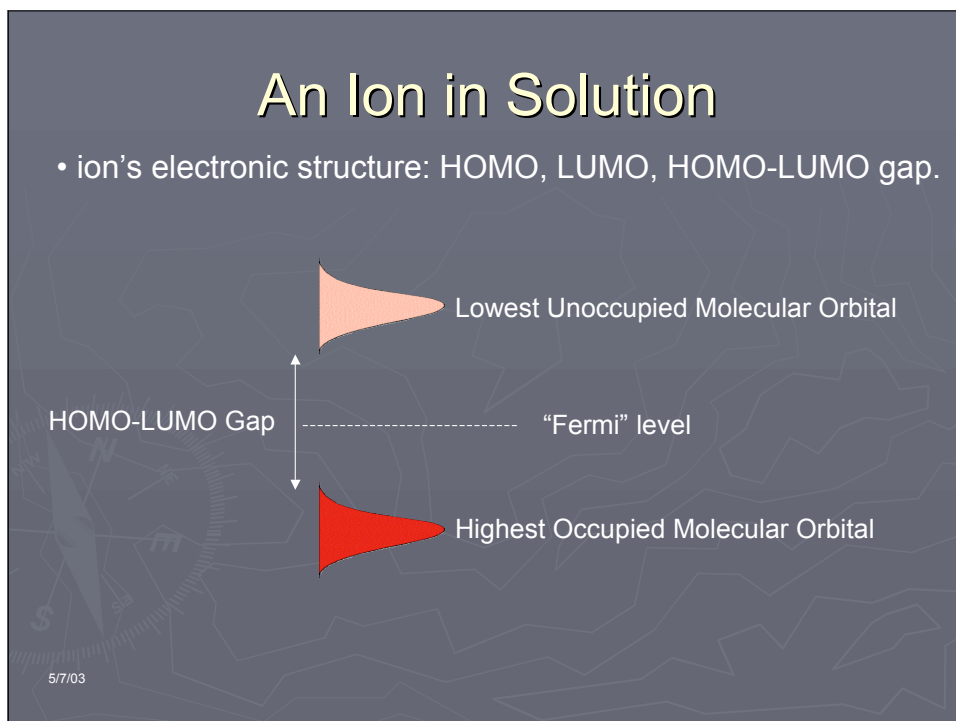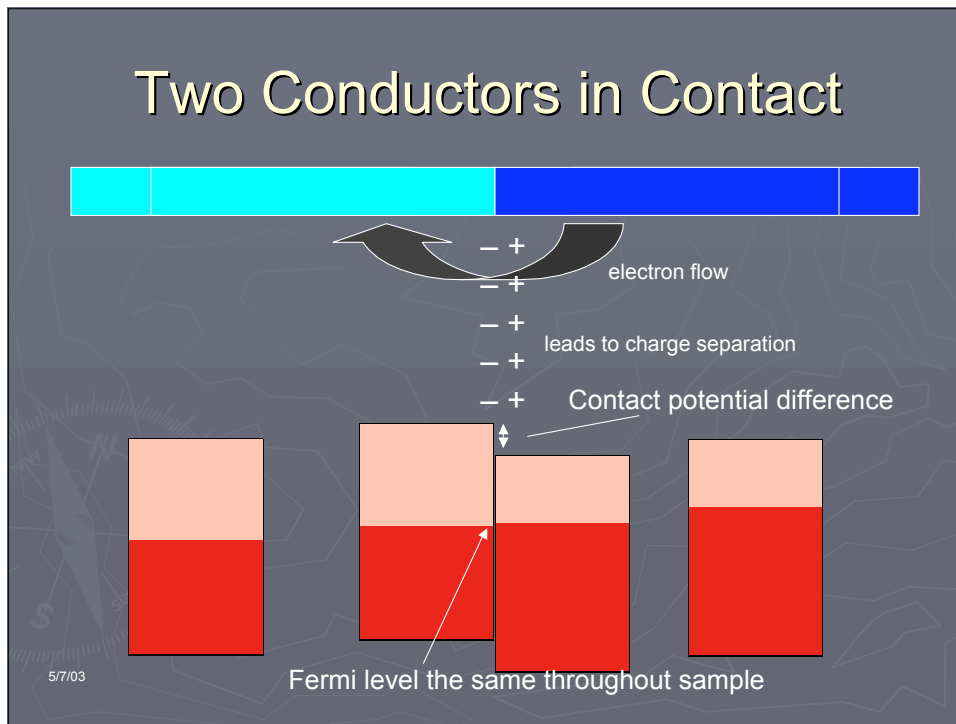5/7/03

Energy Levels

E = 0

Energy

Empty
States

Filled
States

LUMO

HOMO

Vacuum
Level

Fermi
Level

An Atom

A Small
Molecule

A Large
Molecule

Bulk
Material

5/7/03 Chemistry is controlled by the states around the filled/empty transition.

Band Structure

Infinitesimal spacing between filled and empty states

Small but non-zero spacing between filled and empty states

Large spacing between filled and empty states

Valence Band

Band Gap

Core Bands

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Metal   Semiconductor   Insulator

Our focus in this course is on metals.

Fermi Level

- focus on the electrons near the filled/empty boundary.
- each material's energy state distribution is unique; different E_F.

Minimum energy to remove electron from sample

E=0 (vacuum level)

E_F (Fermi level)

E_F (Fermi level)

Metal 1   Metal 2

- the closer an electron is to the vacuum level, the weaker it is bound to the solid
- or, the more energetic is the electron

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Two Conductors in Contact

electron flow

leads to charge separation

Contact potential difference

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Fermi level the same throughout sample

An Ion in Solution

• ion's electronic structure: HOMO, LUMO, HOMO-LUMO gap.

Lowest Unoccupied Molecular Orbital

HOMO-LUMO Gap   ----------------------------   "Fermi" level

Highest Occupied Molecular Orbital

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Metal in an Electrolyte Solution

Fermi levels
are aligned

+ –
+ –
+ –

Charge is transferred to
equilibrate Fermi levels,
producing a charge
separation and a contact
5/7/03 potential difference.

Two Electrolyte Solutions

"Fermi" level

A charge separation
arises to align the
"Fermi" level and
produces a potential
at the interface.

+ –

+ –

+ –
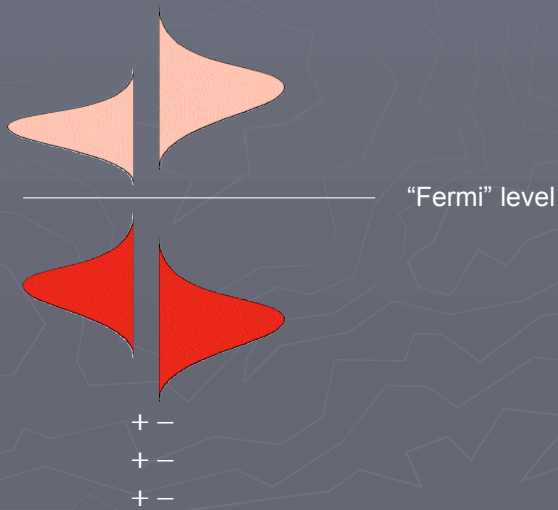
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Junction Potentials

- In any circuit there are junction potentials whenever two dissimilar materials come into contact.

- We focus on the metal-solution interface in electrochemistry

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Electrochemical Thermodynamics

Every substance has a unique propensity to contribute to a system's energy. We call this property **Chemical Potential**.

$$\mu$$

When the substance is a charged particle (such as an electron or an ion) we must include the response of the particle to an electrical field in addition to its Chemical Potential. We call this **Electrochemical Potential**.

$$\bar{\mu} = \mu + z\,F\,\phi$$

These are perhaps the most fundamental measures of thermodynamics.

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Chemical Potential

Chemical potential (or electrochemical potential if it is charged) is the measure of how all the thermodynamic properties vary when we change the amount of the material present in the system. Formally we can write

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} \qquad\qquad \mu = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

$$\mu = \left(\frac{\partial H}{\partial n}\right)_{S,P} \qquad\qquad \mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

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Gibbs Free Energy

The free energy function is the key to assessing the way in which a chemical system will spontaneously evolve.

$$dG = -S\,dT + V\,dP + \sum \mu_i\,dn_i + \gamma\,dA + f\,dl$$

constant T

constant P   don't change
                     shape

don't stretch it

$$dG = \sum \mu_i\,dn_i$$

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Gibbs Function and Work

• Start with the First Law of Thermodynamics and some standard thermodynamic relations. We find

$$dU = dq + dw$$

$$dq = T\,dS$$

$$dw = -P\,dV + dw_{electrical}$$

$$dU = T\,dS - P\,dV + dw_{electrical}$$

$$dH_P = dU_P + P\,dV$$

$$
\begin{aligned}
dG_T &= dH_T - T\,dS \\
&= dU_{T,P} + P\,dV - T\,dS \\
&= T\,dS - P\,dV + dw_{electrical} + P\,dV - T\,dS
\end{aligned}
$$

$$dG_{T,P} = dw_{electrical}$$

And therefore, the Gibbs function is at the heart of electrochemistry, for it identifies the amount of work we can extract electrically from a system.

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Gibbs and the Cell Potential

• Here we can easily see how this Gibbs function relates to a potential.

$$w_{electrical} = VQ$$

$$\text{since} \quad Q = nF$$

$$= nFE$$

• By convention, we identify work which is negative with work which is being done by the system on the surroundings. And negative free energy change is identified as defining a spontaneous process.

$$\Delta G_{T,P} = -w_{electrical} = -nFE$$

• Note how a measurement of a cell potential directly calculates the Gibbs free energy change for the process.

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Standard Reference States

All thermodynamic measurements are of differences between states; there is no absolute value for any property (exception: entropy does have an absolute measure from theory, but it's the only one).

In order to quantify thermodynamics, we choose by convention a reference state. Most common choice is called "Standard Ambient Temperature and Pressure (SATP)".

Temperature = 298 K (25 ˚C)

Pressure = 1 bar (10^5 Pa)

Concentration = 1 molal (mol of solute/kg of solvent)

BUT…

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Standard Reference States

• atmosphere is a widely used unit of pressure.
• 1 atm = 1.0134 bar

Reference State for Pressure is usually 1 atm

• molality better than molarity
• solvent density is T dependent
• volume changes with T

Reference states are indicated by superscript ˚
C˚   or   P˚

But…
• volume is easier to measure than mass
• density of water (the most common solvent) is close to 1

The most commonly used reference state is that of 1 M (mol/liter).

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Activity

The propensity for a given material to contribute to a reaction is measured by **activity, a**.

How "active" is this substance in this reaction compared to how it would behave if it were present in its standard state?

• activity scales with concentration or partial pressure.

$$a \propto C/C° \quad OR \quad a \propto P/P°$$

BUT…
• intermolecular interactions
• deviations from a direct correspondence with pressure or concentration

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Activity Coefficients

Definition of activity

$$a = \gamma \frac{C}{C°} \qquad\qquad a = \gamma \frac{P}{P°}$$

Activity coefficients close to 1 for dilute solutions and low partial pressures.

• it changes with concentration, temperature, other species, etc. Can be very complex.

Generally, we ignore activity coefficients for educational simplicity, but careful work will require its consideration.

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Approximate Activity

• activity is unitless

• activity coefficient is complex over wide ranges of conditions

Since
     — activity coefficients are close to 1 for dilute solutions
     — reference states for partial pressure and concentration have
     numerical value of 1

Therefore, we often approximate activity by concentration (M) or partial
     pressure (atm).

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Solids, Solvents, Liquids

• SOLID: reference is itself

• PURE LIQUID: reference is itself

• SOLVENT: reference is itself

                              a = 1 for all of these materials

Increase amount of these : reaction goes longer, but not faster.

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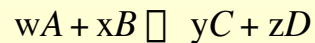
Chemical Potential and Activity

How does chemical potential change with activity?

Integration of the expressions for the dependence of amount of material on the Gibbs function, leads to the following relationship:

$$\mu = \mu^{\circ} + RT \ln a$$

Reaction Quotient

$$wA + xB \rightarrow yC + zD$$

In order to analyze a chemical process mathematically, we form this reaction quotient.

$$Q = \frac{a_C^y \, a_D^z}{a_A^w \, a_B^x}$$

• it always has products in the numerator and reactants in the denominator

• it explicitly requires the activity of each reaction participant.

• each term is raised to the power of its stoichiometric coefficient.

Simplifying Approximations

• Leave out terms involving solids, pure liquids, and solvents

• Solutes appear as the concentration (in M).

• Gases appear as the partial pressure (in atm).

REACTION QUOTIENT IS UNITLESS.

But its value does depend upon the chosen reference state.

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Concentration Dependence

How does Gibbs free energy change with activity (concentration)?

Same dependence as with the chemical potential. We have

$$G = G^{\circ} + RT \ln a$$

When we apply this to a reaction, the reaction quotient comes into to play, giving us

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

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Equilibrium

$$\Delta G = \Delta G^\circ + RT \ln Q$$

When all participants have unit activity (a=1), then Q=1 and ln Q = 0.

$$\Delta G = \Delta G^\circ$$ (duh! As designed.)

Reaction proceeds, Q changes, until finally ΔG=0. The reaction stops.
This is equilibrium.

$$0 = \Delta G^\circ + RT \ln Q^*$$

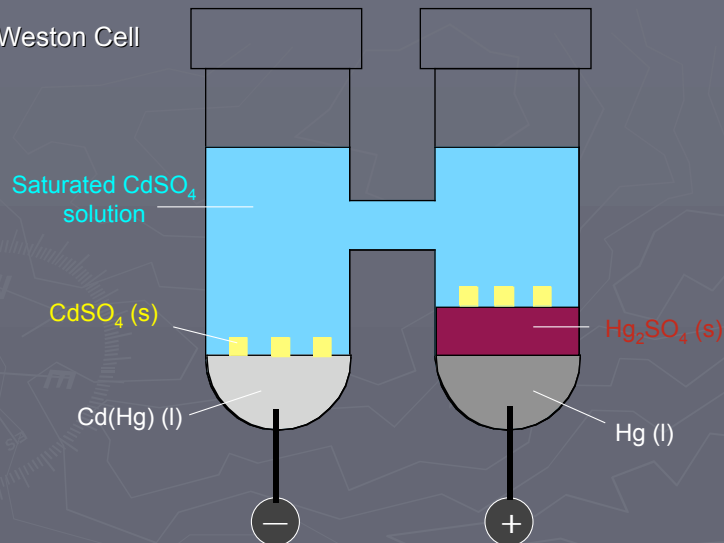$$\therefore \quad \Delta G^\circ = -RT \ln Q^* \qquad\qquad Q^* \equiv K_{eq}$$

This special Q* (the only one for which we achieve this balance) is
renamed K_{eq}, the equilibrium constant.

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An Electrochemical Cell

The Weston Cell

Saturated CdSO$_4$
solution

CdSO$_4$ (s)

Hg$_2$SO$_4$ (s)

Cd(Hg) (l)

Hg (l)

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$-$ $+$

Weston Cell Reactions

Here are the two reactions that are occurring. In the left-hand cell we find

$$Cd(Hg) \longrightarrow Cd^{2+}(aq) + 2e^-$$

• Cd is being oxidized (its oxidation number is going from 0 to +2)

 In the right-hand cell we find

$$Hg_2SO_4(s) + 2e^- \longrightarrow 2\ Hg(l) + SO_4^{2-}(aq)$$

 • Hg is being reduced (its oxidation number is going from +1 to 0)

 The overall reaction is the sum of these two reactions

$$Cd(Hg) + Hg_2SO_4(s) \longrightarrow 2\ Hg(l) + Cd^{2+}(aq) + SO_4^{2-}(aq)$$
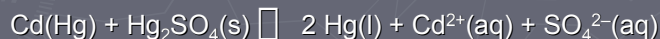
This reaction occurs spontaneously as written. Its free energy change ΔG
is therefore –ive and its cell potential E is +ive.

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Cell Notation

A shorthand cell notation has been developed for convenience. The
    Weston cell is written as

$$Cd(12.5\%\ Hg\ amalgam)\ |\ CdSO_4(aq,\ sat)\ |\ Hg_2SO_4\ (s)\ |\ Hg(l)$$

• write components in sequence
• separate phases with a single vertical line "|"
• a salt bridge or membrane is represented by a double vertical line "||"
• included a specification of the species concentration
• note that the solid $CdSO_4$ is necessary to maintain a saturated solution,
    but it does not participate directly in the reaction so it is not included in
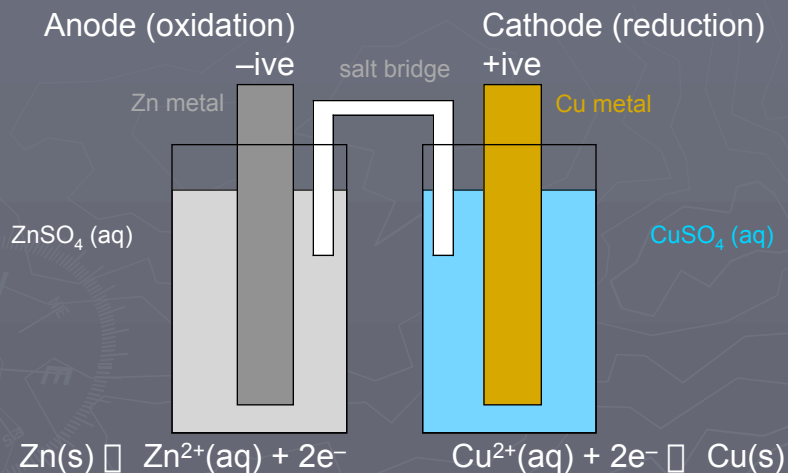   the cell definition

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Electrode Convention

The electrode at which oxidation is occurring is called the anode.

The electrode at which reduction is occurring is called the cathode.

• write the anode on the left and the cathode on the right.
• a cell operating spontaneously in this configuration is said to have a positive total cell potential.
• when connecting a voltmeter, connect the positive terminal to the positive electrode. If it reads a positive potential, you have correctly identified all the terminals. If you read a negative potential, then you have misidentified the reactions in the cells, and you have hooked it up backwards. Reverse your assignment of anode and cathode.
• in a galvanic cell the cathode is +ive
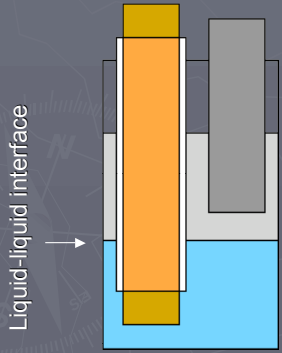• in an electrolytic cell the cathode is –ive.

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Daniell Cell

Anode (oxidation)   Cathode (reduction)
–ive   salt bridge   +ive

Zn metal   Cu metal

$ZnSO_4$ (aq) $CuSO_4$ (aq)

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

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Salt Bridge

What is the role of the salt bridge?

Salt bridge makes cell construction and operation easier.

Daniell Cell without salt bridge

Liquid-liquid interface

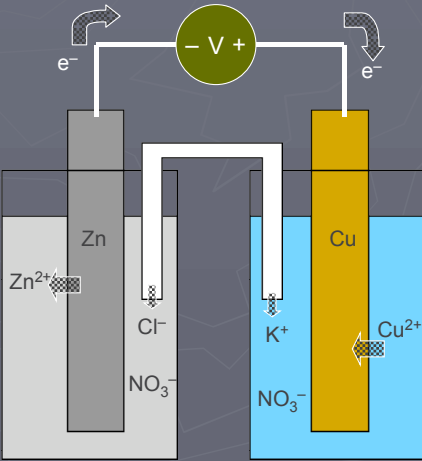Carefully merge two solutions. Make $CuSO_4$ more dense than $ZnSO_4$. Sheath Cu electrode in glass.

Pack tube with a viscous, aqueous solution of KCl or KNO_3. The viscosity prevents mixing with the electrolytes. The ions permit exchange of charge. The chosen ions have similar mobility to minimize junction potentials.
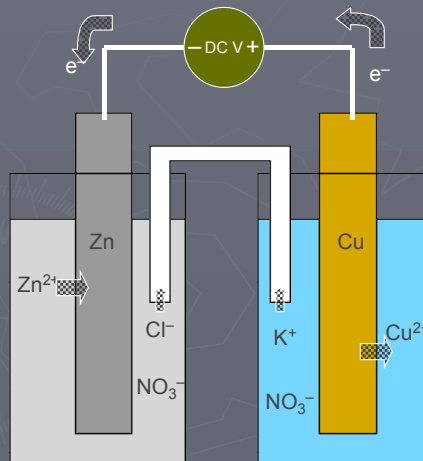
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Flow of Charge

How does charge flow in a cell?

If concentrations are 1M, then the cell is at standard conditions and the measured potential is +1.10 V.

– V +

e^- e^-

Zn   Cu

Zn^{2+}

Cl^-

K^+ Cu^{2+}

NO_3^-

NO_3^-

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Electrolytic Cell

What about running the cell in reverse?

− DC V +

e⁻   e⁻

Zn   Cu

Zn²⁺⇨

Cl⁻

NO₃⁻

K⁺   Cu²⁺

NO₃⁻

• apply an external voltage of opposite polarity.
• magnitude must exceed the +1.10 V that the cell produces on its own.
• Cu electrode now dissolves and Zn now plates out on its electrode.

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Nernst Equation

Take the expression for the Gibbs dependence on activity and turn this around for an expression in terms of the cell potential.

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

The relation between cell potential E and free energy gives

$$-nFE = -nFE^{\circ} + RT \ln Q$$

Rearrange and obtain the Nernst Equation.

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

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Nernst Equation continued

The equation is sometimes streamlined by restricting discussion to T = 25 °C and inserting the values for the constants, R and F.

$$E = E^\circ - \frac{0.0257}{n} \ln Q$$
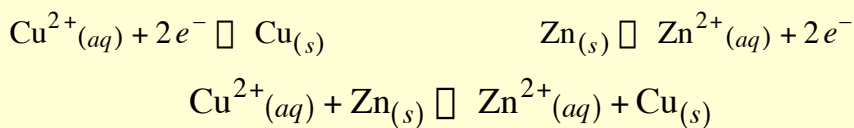
$$E = E^\circ - \frac{0.0592}{n} \log Q$$

Note the difference between using natural logarithms and base10 logarithms.

Be aware of the significance of "n" – the number of moles of electrons transferred in the process according to the stoichiometry chosen.

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Example: Daniell Cell

Cu is cathode (it is reduced). Zn is anode (it is oxidized).

$$\mathrm{Cu}^{2+}{}_{(aq)} + 2\,e^- \rightarrow \mathrm{Cu}_{(s)} \qquad\qquad \mathrm{Zn}_{(s)} \rightarrow \mathrm{Zn}^{2+}{}_{(aq)} + 2\,e^-$$

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

Note that n=2 for this reaction.   =1

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{Cu}\, a_{Zn^{2+}}}{a_{Cu^{2+}}\, a_{Zn}} \qquad = \gamma \frac{\left[Zn^{2+} \right]}{[\ ]^\circ}$$

=1

Activity for solid materials is 1; replace activities with concentrations.

$$E = E^\circ - \frac{RT}{2F} \ln \left[\frac{\mathrm{Zn}^{2+}}{\mathrm{Cu}^{2+}} \right] = 1.10 - 0.0128_5 \ln \left[\frac{\mathrm{Zn}^{2+}}{\mathrm{Cu}^{2+}} \right]$$

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Example <small>continued</small>

What is the potential in the cell if $[Cu^{2+}] = 0.01$ M and $[Zn^{2+}] = 1.00$ M?

$$E = 1.10 - 0.0128_5 \ln \frac{1.00}{0.01} = 1.10 - 0.0128_5 \ln(100)$$

$$= 1.10 - 0.0128_5 (4.6052) = 1.041 \, V$$

Note that the cell potential decreased by about 60mV. This was a change in concentration of TWO orders of magnitude, but since it was also a 5/7/03 TWO electron process, we saw the same 60 mV change in potential.

Example: Weston Cell

Recall that the total cell reaction is

$$Cd(Hg) + Hg_2SO_4(s) \longrightarrow 2\, Hg(l) + Cd^{2+}(aq) + SO_4{}^{2-}(aq)$$
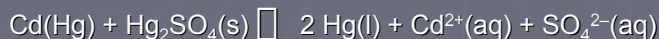
and it is a two electron process. The Nernst equation is

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{Hg}^2 \, a_{Cd^{2+}} \, a_{SO_4^{2-}}}{a_{Cd} \, a_{Hg_2SO_4}}$$

The activity of liquid Hg is 1; that for solid Hg_2SO_4 is 1; that for Cd^{2+} and $SO_4{}^{2-}$ will be constant since the solution remains saturated (continual precipitation or dissolution of solid $CdSO_4$ as necessary). The Cd concentration in the amalgam (at 12.5%) will not change much if the cell current is kept low.

$E =$ 1.0180 V at 25 ˚C (NOT standard state, but a very stable output). 5/7/03

Concentration Cell

Nernst equation demonstrates that potential depends upon concentration.

A cell made of the same materials, but with different concentrations, will also produce a potential difference.

$$Cu \mid Cu^{2+} (0.001\ M) \parallel Cu^{2+} (1.00\ M) \mid Cu$$

What is standard cell potential E˚ for this cell?

What is the cell potential E?   What is "n", the number of electrons transferred? Which electrode, anode or cathode, will be in numerator?

$$E = E^\circ - \frac{0.0257}{n} \ln\left(\frac{\left[Cu^{2+} \right]_{anode}}{\left[Cu^{2+} \right]_{cathode}} \right)$$
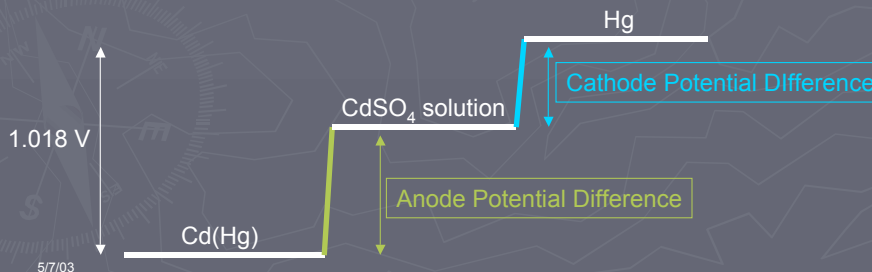
$$= 0 - \frac{0.0257}{2} \ln\left(\frac{0.001}{1.00} \right) = +0.089\ V$$

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Half-Cell Potentials

It is best to think of a cell's operation in terms of the two reactions taking place at the two electrodes separately.

• can understand each half-cell reaction in isolation

• makes classifying and tabulating data easier

Hg

Cathode Potential DIfference

CdSO$_4$ solution

1.018 V

Anode Potential Difference

Cd(Hg)

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Standard Reduction Potentials

Convention: We discuss half-cell reactions from a point of view of their being reduction processes.
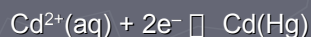
Weston Cell Cathode:

$$Hg_2SO_4(s) + 2e^- \rightarrow 2\ Hg(l) + SO_4^{2-}(aq)$$

This is a reduction and is the half-cell process we consider.

Weston Cell Anode:

$$Cd(Hg) \rightarrow Cd^{2+}(aq) + 2e^-$$

This is an oxidation. We must consider the reverse process in our convention.

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(Hg)$$

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Nernst and Half-Cells

The Nernst equation can be accurately applied to the half cell reactions. The same rules of "products over reactants" applies to forming the activity ratio in the logarithm. The number of electrons is as specified by the stoichiometry.

The reactions in the Weston Cell:

$$Hg_2SO_4(s) + 2e^- \rightarrow 2\ Hg(l) + SO_4^{2-}(aq)$$

$$E_{Hg_2SO_4/Hg} = E^{\circ}_{Hg_2SO_4/Hg} - \frac{RT}{2F}\ln\left(\frac{a_{Hg}^2\ a_{SO_4^{2-}}}{a_{Hg_2SO_4}} \right)$$

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(Hg)$$
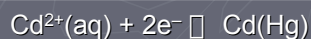
$$E_{Cd^{2+}/Cd} = E^{\circ}_{Cd^{2+}/Cd} - \frac{RT}{2F}\ln\left(\frac{a_{Cd}}{a_{Cd^{2+}}} \right)$$

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So What Is The Half-Cell E°?

To complete each Nernst equation we need to know the potential difference between each electrode and the solution. This we cannot measure directly.
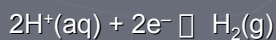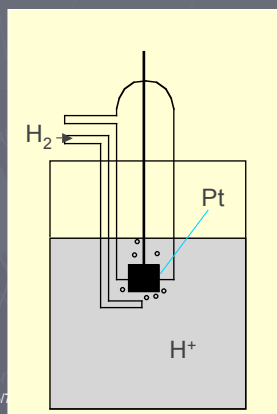
?

Hg

?

CdSO$_4$ solution

Cd(Hg)
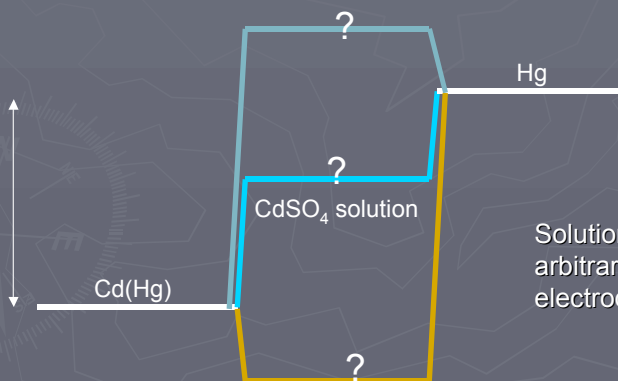
Solution: Adopt an arbitrary reference electrode.

?

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Standard Hydrogen Electrode

The convention is to select a particular electrode and assign its standard reduction potential the value of 0.0000V. This electrode is the Standard Hydrogen Electrode.

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

H$_2$

Pt

The "standard" aspect to this cell is that the activity of H$_2$(g) and that of H$^+$(aq) are both 1. This means that the pressure of H$_2$ is 1 atm and the concentration of H$^+$ is 1M, given that these are our standard reference states.

H$^+$

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Standard as a Reference

Once chosen, this reference cell is employed as one half-cell with all other cells. Since its potential is assigned the value of 0.000 V, all of the potential difference measured experimentally is attributed to the other, test electrode.

Since we are cataloguing reduction potentials, the cells are formed by connecting the Standard Hydrogen Electrode (SHE) as the anode and the other half-cell as the cathode.

Consider:

$$Pt \mid H_2 \text{ (1.00 atm)} \mid H^+ \text{ (1.00 M)} \parallel Cu^{2+} \text{ (1.00 M)} \mid Cu$$

Measured potential = +0.340 V

Since the activity of all components in the Cu cell are standard, +0.340 V is the **STANDARD REDUCTION POTENTIAL** of the Cu^{2+}/Cu couple.

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By Contrast…

Consider the Zn^{2+}/Zn half-cell.

$$Pt \mid H_2 \text{ (1.00 atm)} \mid H^+ \text{ (1.00 M)} \parallel Zn^{2+} \text{ (1.00 M)} \mid Zn$$

Measured Cell Potential = -0.7626 V

This is the Standard Reduction Potential for this couple.

• negative potential means it really is being oxidized

• convention accounts for that with the negative sign when written as a reduction.

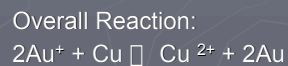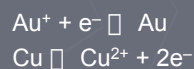• will make for easier use of tables.

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Standard Potential Tables

All of the equilibrium electrochemical data is cast in Standard Reduction Potential tables.

$F_2 + 2e^- \rightarrow 2F^-$	+2.87	$2H^+ + 2e^- \rightarrow H_2$	0.0000
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^+ + e^- \rightarrow Au$	+1.69	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61	$In^{3+} + 3e^- \rightarrow In$	-0.34
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$Ag^+ + e^- \rightarrow Ag$	+0.80	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	$V^{2+} + 2e^- \rightarrow V$	-1.19
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22	$Cs^+ + e^- \rightarrow Cs$	-2.92
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15	$Li^+ + e^- \rightarrow Li$	-3.05

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Using the Tables

$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15

• choose one reaction for reduction
• choose another for oxidation

$Au^+ + e^- \rightarrow Au$
$Cu \rightarrow Cu^{2+} + 2e^-$

Overall Reaction:
$2Au^+ + Cu \rightarrow Cu^{2+} + 2Au$

Cell potential E:
E = +1.69 - 0.34 = +1.35 V

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Using the Tables continued

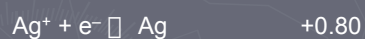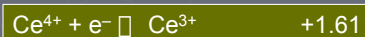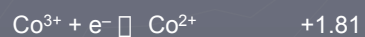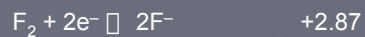|	
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15

• choose one reaction for reduction
• choose another for oxidation

$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$
$Ce^{3+} \rightarrow Ce^{4+} + e^-$

Overall Reaction:
$Sn^{4+} + 2Ce^{3+} \rightarrow Sn^{2+} + 2Ce^{4+}$

Cell potential E:
E = +0.15 - 1.61 = -1.46 V

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Calculating Cell Potential

Because we tabulate reduction potentials, the cell potential is calculated (from those tabulated numbers) as

$$E_{cell} = E_{cathode} - E_{anode}$$

The minus sign is present only because we are using reduction potential tables and, by definition, an anode is where oxidation occurs.
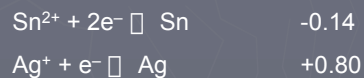
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Example

$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$V^{2+} + 2e^- \rightarrow V$	-1.19

To get a final positive cell potential, the more negative half-reaction (V) must act as the anode.

$Fe^{2+} + V \rightarrow Fe + V^{2+}$

E_{cell} = -0.44 - (-1.19) = +0.75 V

$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$Ag^+ + e^- \rightarrow Ag$	+0.80

More negative potential reaction is the anode.

Multiply the Ag reaction by 2, but don't modify the cell potential.

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

E_{cell} = +0.80 - (-0.14) = +0.94 V

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Oxidative Strength

$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
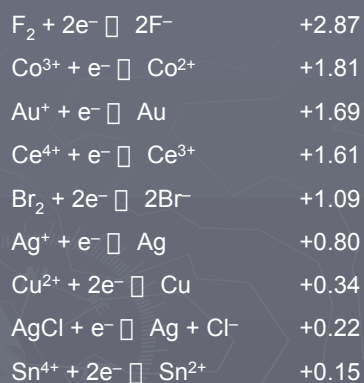
Consider a substance on the left of one of these equations. It will react as a reactant with something below it and on the right hand side.

• higher in the table means more likely to act in a reducing manner.

• when something is reduced, it induces oxidation in something else.

• it is an oxidizing agent or an oxidant.

• F_2 is a stronger oxidant than Ag^+.

• Cu^{2+} is a weaker oxidant than Ce^{4+}.

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Reductive Strength

$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15

Substances on the right hand side of the equations will react so as to be oxidized.

• LOWER in the table means a greater tendency to be oxidized.

• when oxidized, it induces reduction in something else. It is a reducing agent or reductant.

 • Ag is a stronger reductant than Au.

• Co^{2+} is a weaker reductant than Sn^{2+}

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Cell Potentials, Gibbs Free Energy and Equilibrium Constants

The equations we have allow is to relate measured cell potentials to Standard Gibbs Free Energies of reaction. These in turn are related to a reaction's equilibrium constant.

Consider the cell

Pt | I$^-$ (1.00 M), I$_2$ (1.00 M) || Fe^{2+} (1.00 M), Fe^{3+} (1.00 M) | Pt

Standard Cell Potential is (from tables) = 0.771 V - 0.536 V = +0.235 V

$$\Delta G^\circ = -nFE^\circ = -2\left(96285\ \frac{C}{mol}\right)(0.235\ J) = -45,348\ \frac{J}{mol}$$

This is the free energy change. It leads to the equilibrium constant for the reaction.

$$\ln K_{eq} = -\frac{\Delta G^\circ}{RT} = -\frac{\left(-45348\ \dfrac{J}{mol}\right)}{\left(8.314\ \dfrac{J}{K\ mol}\right)(298\ K)} = 18.3034$$

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$$K_{eq} = e^{18.3034} = 8.89 \times 10^7$$

Formal Potentials

• standard states are impossible to achieve

• theoretical calculations of activity coefficients possible below 10^{-2} M.

• formal potential is that for the half-cell when the **concentration quotient** in the Nernst equation equals 1.

• solution with a high concentration of inert electrolyte, activity coefficients are constant. Use formal potentials which are appropriate for that medium and molar concentrations for very accurate work.

• often specified as occurring in 1.0 M $HClO_4$, 1.0 M HCl, or 1.0 M H_2SO_4.

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Example

Consider the Fe(III)/Fe(II) couple. The Nernst equation reads

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{F}\ln\left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right) = E^{\circ}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{F}\ln\left(\frac{\gamma_{Fe^{2+}}[Fe^{2+}]}{\gamma_{Fe^{3+}}[Fe^{3+}]}\right)$$

$$= E^{\circ}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{F}\ln\left(\frac{\gamma_{Fe^{2+}}}{\gamma_{Fe^{3+}}}\right) - \frac{RT}{F}\ln\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

When the concentration quotient is 1, the last term is 0. This defines the new formal potential as

$$E^{\circ'} = E^{\circ}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{F}\ln\left(\frac{\gamma_{Fe^{2+}}}{\gamma_{Fe^{3+}}}\right)$$

This new reference potential is constant, because the activity coefficients are constant because they are controlled by the huge excess of inert ions.

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Example continued

The standard reduction potential for the Fe(III)/Fe(II) couple is

$$E° = 0.771 \text{ V}$$

In 1.0 M $HClO_4$ it is

$$E°'(1.0 \text{ M } HClO_4) = 0.732 \text{ V}$$

In 1.0 M HCl it is

$$E°'(1.0 \text{ M HCl}) = 0.700 \text{ V}$$

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Some Extra Work For You

• First Year Chemistry Textbook

• read chapter on electrochemistry.

• lots of examples and problems in using standard reduction potential tables

• interrelating E, E°, concentrations (Nernst equation)

• interrelating E°, ΔG, and K_{eq}.

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