Announcements

Mid-Term Exam

When and Where

• Saturday, November 3, 7:00 – 9:00 PM. Since we will start setting up about half an hour prior to the exam, please remain outside of the rooms, as they cannot be used for studying while we set up.

• Assigned rooms are based on the lecture section of registration and the **last five digits of the student number**. You ***must*** write in the assigned room, as space is limited. Those who arrive at the incorrect room will be asked to leave.

Section 003 (Lipson)	Room
04620 – 14942	SH 2355
15176 – 21129	SH 3315
21169 – 27343	SH 3317
27350 – 40575	TH 3101
40576 – 99554	TH 3102

Section 006 (Lipson)	Room
01806 – 15307	HSB 236
15315 – 27190	HSB 240
27250 – 98264	HSB 35

TH = Thames Hall
HSB = Health Sciences Building
SH = Sommerville House

I have been told that the biochem instructor said that he has made an announcement multiple times about an early 280a write on Thursday for those with conflicts with C020. Therefore, this conflict will no longer be used as a valid reason to miss the Chemistry midterm.

The cell can be written using the following notation:

Salt Bridge

Anode half-cell　　Cathode half-cell

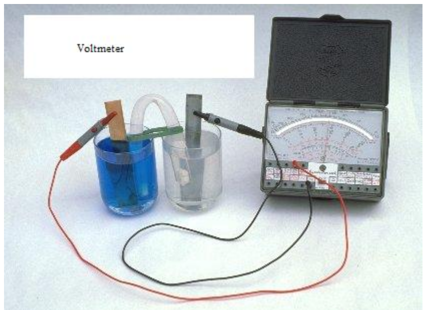
$Zn(s)|\ Zn^{2+}(aq)||\ Cu^{2+}(aq)|Cu(s)$

Electrons flow this way

Phase boundary　　Phase boundary

- By convention, oxidation is on the left, and the reduction is on the right
- Phase boundary refers to the solid metal dipped into aqueous solution

When a voltmeter is used to measure the *EMF*, the **r**ed (positive) wire is connected to the **r**ight or **r**eduction electrode (cathode) where electrons are **r**eceived



If a cell is connected in this manner, a positive voltage indicates that the reaction is proceeding forwards

Experimentally, it is found that the voltage and direction of current flow depends on the electrode materials, temperature and concentration of ions involved.
It is useful therefore to define *standard conditions*.

- Concentration of ions = 1M (for example, 1 M $ZnSO_4$)
- Temperature = 25^{o}C   Pressure = 1 atm

In C020 we will not examine the concentration effect. For those who are interested, read about the Nernst equation M&H p. 486 - 489

Cell potentials measured under standard conditions are referred to as standard cell potentials $\mathbf{E^o_{cell}}$ (sometimes E^o)

2. Standard Electrode Potentials

Any redox process can be split into two half-reactions.
Thus, E^o_{cell} is a sum of the voltages generated by the oxidation half-reaction (at the anode) and the reduction half-reaction (at the cathode).

$$E^o_{cell} = E^o_{ox} + E^o_{red}$$

Electrons move through the wire from one side to the other because the two sides differ in potential energy (voltage)

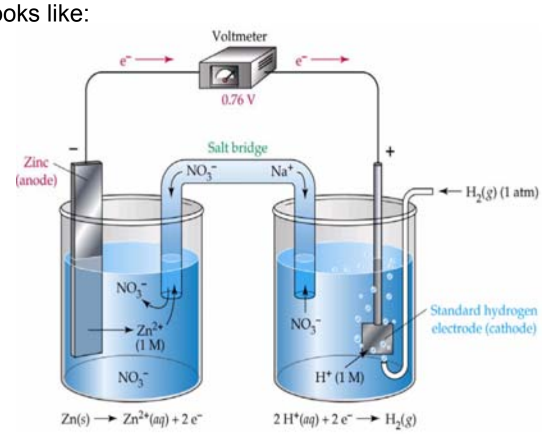
Where do we get the potentials for the E^o_{ox} and E^o_{red} half-reactions?
They can't be measured individually because the e^-s have nowhere to go or to come from

Thus, the half-cell potentials are experimentally determined using the standard hydrogen electrode (**SHE**) as a reference.
Since we're dealing with a gas, we use an inert electrode (like platinum)

By definition the standard potential of SHE is **ZERO**
$2H^+$ (one molar) + $2e^-$ $\rightarrow$ $H_2(g)$ (1 atm) $E^0_{red} = 0.000$ V

E^o_{red} and E^o_{ox} for the species are related as $E^o_{red} = -E^o_{ox}$
$H_2(g)$ (1 atm) $\rightarrow$ $2H^+$(one molar) + $2e^-$ $E^o_{ox} = 0.000$ V

So, to determine the value of a standard potential for zinc, we need to construct a cell that looks like:



The value of E^o_{cell} is +0.762 V when the voltmeter is connected properly (positive side to the cathode).
In this case the cathode is the hydrogen side which means that H^+ is being reduced to H_2

Likewise Zn is being oxidized at the anode side

Thus, E^o_{cell} = +0.762 V = E^o_{red} + E^o_{ox}

By definition, E^o_{red} of the SHE = 0 V so E^o_{ox} = +0.762 V

However it must be remembered that E^o_{ox} corresponds to the oxidation of Zn(s)

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

Since $E^o_{red} = -E^o_{ox}$ we can write the following: essentially flip the reaction to get the reduction potential

$Zn^{2+} + 2e^- \rightarrow Zn(s)$ E^o_{red} = -0.762 V

Thus, if electrons were present in the reference cell comprised of zinc and SHE they have a choice. Will they go to H^+ or will they go to $Zn^{2+?}$

$Zn^{2+}(aq) + 2e^- \rightarrow$ E^o_{red} = -0.762

$2H^+(1M) + 2e^- \rightarrow H_2(g)(1\ atm)$ E^o_{red} =0.000 V

When written as reduction half-reactions, the reaction that will occur is the one with the most positive potential

In this case, H^+ is preferentially reduced over Zn^{2+}.

Corollary: H^+ is a stronger oxidizing agent than Zn^{2+}.

In other words, H^+ is capable of oxidizing Zn(s)

This is observed experimentally in the Zn/SHE system

A table of standard electrode potentials, shown as reduction half-reactions, is provided in the tutorial manual.
When comparing any two half-reactions, the one that will proceed as written will have the highest potential E^o_{red}.
The other half-reaction will need to be reversed to obtain E^o_{ox}.

Some common E^o_{red} values and reactions are shown here. Remember, the higher the value, the more likely the reduction will occur.

TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

- We showed how the $Zn^{2+}|Zn$ half-potential was determined.

All half-potentials of all the other species in the table above were determined in the same way: by comparing against the SHE

- To construct a cell using any two of the reduction half-potentials, one must be reversed to correspond to an oxidation.

Returning to the Cu/Zn cell, it is clearer now why the reaction was written as:
(Zn oxidized; Cu^{2+} reduced)

Cell notation: $Zn|Zn^{2+}||Cu^{2+}|Cu$

From the table we have the relevant potentials:

$Zn^{2+} + 2e^- \rightarrow Zn$ $\quad E^o_{red} = -0.76$ V

$Cu^{2+} + 2e^- \rightarrow Cu$ $\quad E^o_{red} = +0.34$ V

The most positive reduction potential is the one that occurs, which is the one with Cu involved.
This is because Cu^{2+} is more likely to be reduced than Zn^{2+} or Cu^{2+} is a stronger oxidizing agent.

Since Cu^{2+} is the species being reduced, we must flip the zinc reduction half-reaction to convert it to an oxidation.

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad E^o_{ox} = +0.76 \text{ V}$$

Therefore, $E^o_{cell} = E^o_{red} + E^o_{ox} = +0.34 + 0.76 = +1.10$ V

Because E^o_{cell} is positive, the reaction will go as written;
that is, the reaction will be spontaneous

How about the cell?: $Cu|Cu^{2+}||Zn^{2+}|Zn$

$$Zn^{2+} + 2e^- \rightarrow Zn \quad E^o_{red} = -0.76 \text{ V}$$
$$Cu \rightarrow Cu^{2+} + 2e^- \quad E^o_{ox} = -0.34 \text{ V}$$

This cell potential would be -1.10 V, which means the reaction would not proceed as written spontaneously.
In fact the reverse would occur.