

Fall out from the November Term Test



- At least one student was not allowed to use a non-legal calculator. Be aware: The **only** calculator allowed in C020 is the Sharp EL-510R(B)
- There were reports of students talking before the TAs released you from the test. As we can not control the conversation in the future this will be taken as cheating. Listen to the proctors.
- Too many people did not fill out which exam code. This meant a lot of work to find out what it was. Please be more careful.
- Some people did not fill out their student number correctly.
- It doesn't matter which lecture section you attend but you must write with the one you're registered in!

Section 003



Average = 75.3%

Standard Deviation = 18.1%

Distribution

A+ : 27%

A: 23%

B: 13%

C: 20%

D: 6%

F: 11%

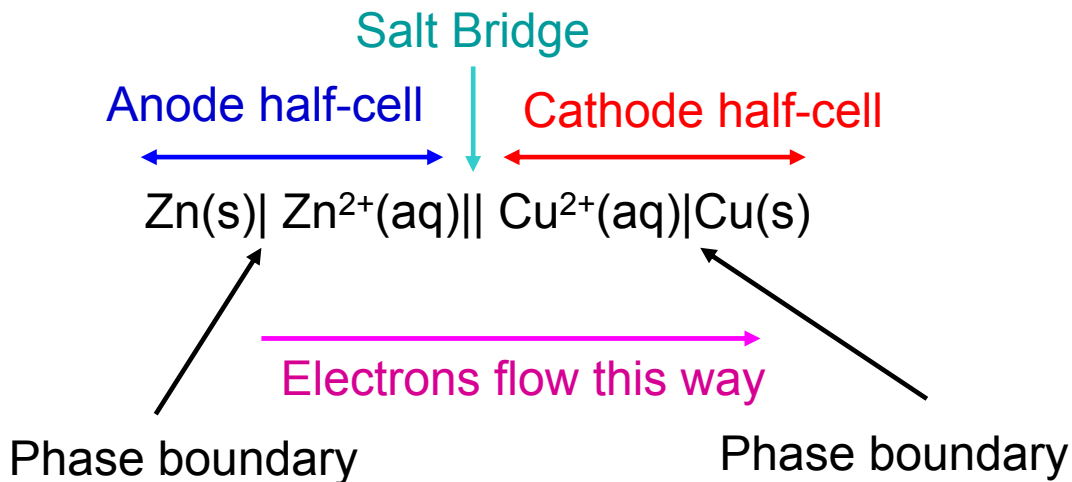
Individual marks should be up soon on Owl WebCT

This is the week of November 5-9, 2007

Group 1: Lab on Redox

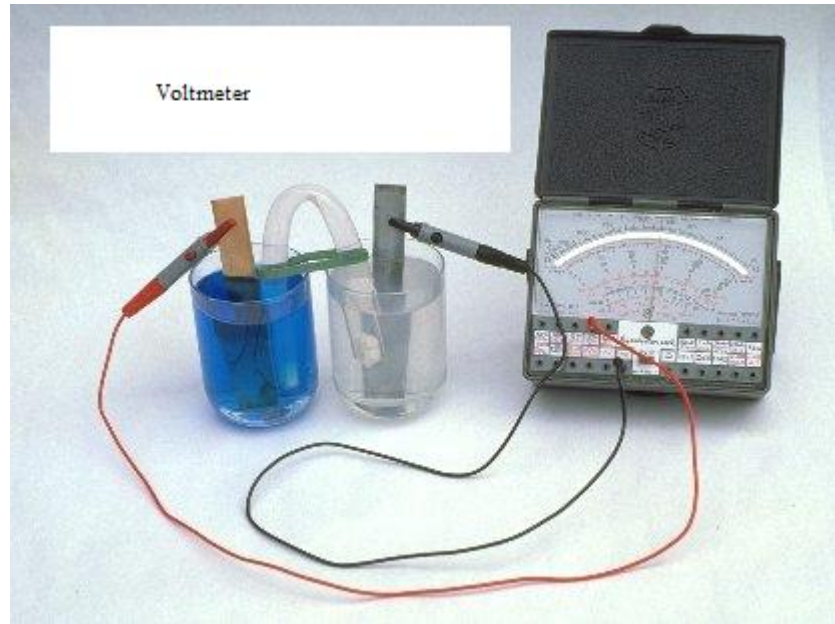
Group 2: Tutorial on Atoms & Periodicity

The cell can be written using the following notation:



- 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 red (positive) wire is connected to the right or reduction electrode (cathode) where electrons are received



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 ZnSO₄)

➤ Temperature = 25°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 E°_{cell} (sometimes E°)

2. Standard Electrode Potentials

Any redox process can be split into two half-reactions.

Thus, E°_{cell} is a sum of the voltages generated by the oxidation half-reaction (at the anode) and the reduction half-reaction (at the cathode).

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$$

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

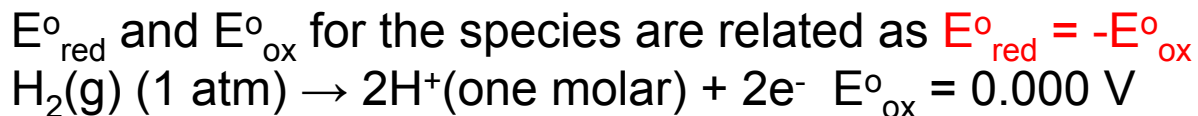
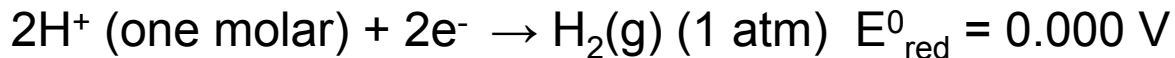
Where do we get the potentials for the E°_{ox} and E°_{red} half-reactions?

They can't be measured individually because the e⁻s have nowhere to go or to come from

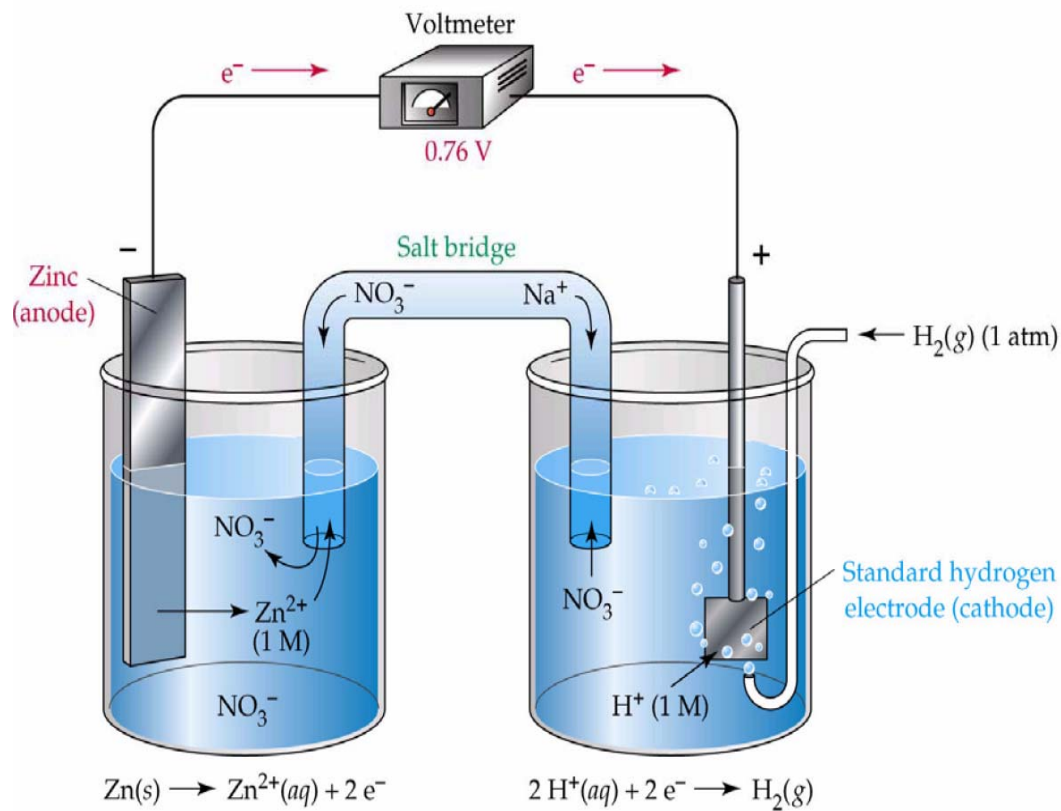
Thus, the half-cell potentials are experimentally determined using the standard hydrogen electrode (**SHE**) as a reference.

Since we're dealing with a gas, we use an inert electrode (like platinum)

By definition the standard potential of SHE is **ZERO**



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



The value of E°_{cell} is +0.762 V when the voltmeter is connected properly (positive side to the cathode).

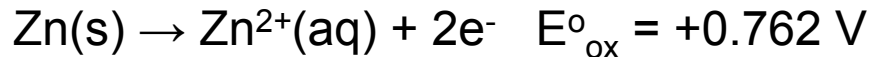
In this case the cathode is the hydrogen side which means that H^+ is being reduced to H_2

Likewise Zn is being oxidized at the anode side

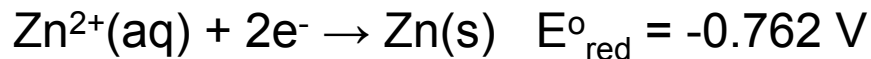
$$\text{Thus, } E^{\circ}_{\text{cell}} = +0.762 \text{ V} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{ox}}$$

$$\text{By definition, } E^{\circ}_{\text{red}} \text{ of the SHE} = 0 \text{ V so } E^{\circ}_{\text{ox}} = +0.762 \text{ V}$$

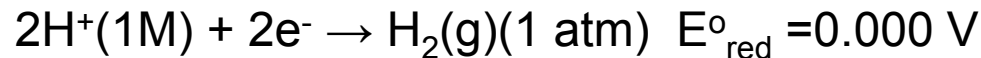
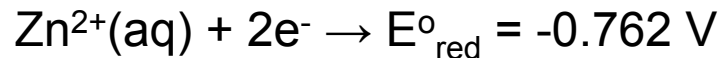
However it must be remembered that E°_{ox} corresponds to the oxidation of Zn(s)



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



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+} ?



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°_{red} .

The other half-reaction will need to be reversed to obtain E°_{ox} .

Some common E°_{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

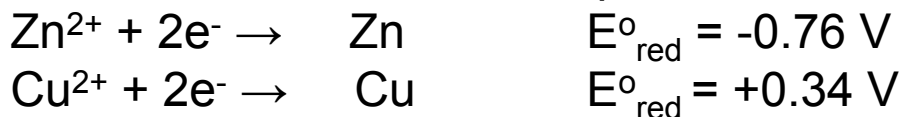
	Reduction Half-Reaction	E° (V)	
 <p>Stronger oxidizing agent</p>	$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}(\text{aq})$	2.87	 <p>Weaker reducing agent</p>
	$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.78	
	$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	1.51	
	$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$	1.36	
	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	1.33	
	$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.23	
	$\text{Br}_2(\text{l}) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$	1.09	
	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	0.80	
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	0.77	
	$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70	
	$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$	0.54	
	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$	0.40	
	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$	0.34	
	$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	0.15	
	$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$	0	
	$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.13	
	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.26	
$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.40		
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.45		
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.76		
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83		
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.66		
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.37		
$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.71		
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.04		
<p>Weaker oxidizing agent</p>			<p>Stronger reducing agent</p>

- We showed how the $\text{Zn}^{2+}|\text{Zn}$ 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: $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$

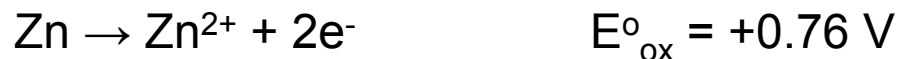
From the table we have the relevant potentials:



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.

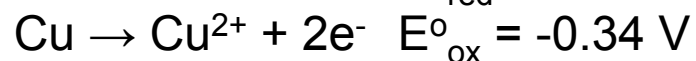
Since Cu^{2+} is the species being reduced, we must flip the zinc reduction half-reaction to convert it to an oxidation.



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

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

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



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

In fact the reverse would occur.