

## Chemistry: Electrochemistry

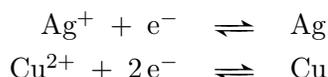
### 3.1 Voltage

1. We now want to quantify the energy we can get from a particular redox reaction in a galvanic cell. We do this in terms of **voltage**.
2. Voltage is the commonly used name for **electrical potential**. Like potential energy (indeed like all energies), voltage needs a reference.
3. We will define this reference later. For now think of voltage as a height above some *arbitrarily defined* reference point. It turns out that only differences or changes in voltage matter, so the reference voltage can be anything as long as we all agree to use the same reference all the time. [Again, we define this reference later in this class.]

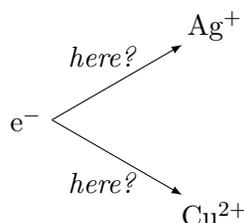
The analogy for reference voltage is the idea of “elevation” of a location on earth. All elevations are reported relative to sea-level. The Dead Sea is the lowest surface elevation in the world measuring at  $-411$  meters (or 411 meters *below* sea-level) and Mt. Everest is the highest measuring at  $+8850$  meters *above* sea-level. Therefore, the difference in elevation between Mt. Everest and the Dead Sea is 9261 meters (this would be true regardless of the reference elevation).

### 3.2 Reductions Only, Please

1. To begin a systematic method study of **cell potential** we need to think of each of the two half-cells as if they are in a battle for electrons.
2. We imagine that each cell wants to be reduced (that is each cell wants to be the cathode... wants those electrons). However, one of the cells is simply better at grabbing electrons than is the other.
3. Consider for example a collection of solid copper, solid silver, copper(II) sulfate, and silver chloride.
4. First, we imagine that both half-reactions are trying to be reduction half-reactions



The question is where do the electrons go?



5. We find that the silver cations  $\text{Ag}^+$  are simply better at grabbing free electrons than the copper cations  $\text{Cu}^{2+}$ .
6. We know this because the voltage for the reduction of  $\text{Ag}^+$  is larger than the voltage for the reduction of  $\text{Cu}^{2+}$ .

The electrons get to lower their energy more by reducing the silver ion rather than the copper ion.

7. Therefore, our process will now involve first a comparison of the reduction potentials  $E$  of the half-cells.

- (a) The half-cell with the LARGER reduction potential  $E$  will win the battle for the electrons and will be reduced and so will become the cathode.
- (b) Sadly, the other half-cell will lose the battle because its  $E$  is smaller, so it will be oxidized, and it becomes the anode.

8. In our example

$$E_{\text{Ag}^+} > E_{\text{Cu}^{2+}}$$

and the silver half-cell is reduced and so becomes the cathode. The copper half-cell is oxidized and so becomes the anode.

9. Finally, we the total potential for the entire cell by SUBTRACTING the potentials of the two electrodes.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

where we

$$\begin{aligned} E_{\text{cathode}}^{\circ} &= \text{reduction potential for cathode half-reaction} \\ E_{\text{anode}}^{\circ} &= \text{reduction potential for anode half-reaction} \end{aligned}$$

10. In the above example,

$$E_{\text{cell}}^{\circ} = E_{\text{Ag}^+}^{\circ} - E_{\text{Cu}^{2+}}^{\circ}$$

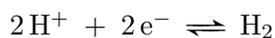
[In reality the copper is the anode and so we subtract its potential. Why? The copper is actually being oxidized so going in the opposite direction.]

11. Finally, in all of the above the  $\circ$  means under standard conditions which means 1.00 M solutions at 25°C with gases at 1 atm. [Don't worry about this detail for this course.]

### 3.3 Hydrogen Standard

In order to calculate  $E^{\circ}$  for anything we need a reference voltage (or height). That is, we need the "sea-level" for electrochemistry.

A long time ago chemists decided that the reduction of hydrogen ions will be the reference



The above is defined to have an electric potential of zero volts  $E^{\circ} \equiv 0$  Volts.

All other potential are tabulated in terms of this in **Tables of Standard Reduction Potentials**. [Your textbook's table is attached.]

### 3.4 Signs

Since the electric reduction potentials are expressed relative to reduction of hydrogen ions to form hydrogen gas, here are some observations possible about the signs.

1. Reduction reactions that have  $E^{\circ}$  that are positive are better at being reduced than  $\text{H}^+$ . They are better at acquiring electrons than  $\text{H}^+$ .
2. An electrode with a positive potential means that hydrogen gas is more willing to give up its electrons than that electrode.
3. A reaction with a negative  $E^{\circ}$  means that reaction is not as good at taking electrons as is  $\text{H}^+$ .

### 3.5 Bottom Line

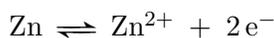
1. The total potential for any cell is always the **standard reduction potential** of the cathode minus the **standard reduction potential** of the anode.
2. If the total cell's potential is positive, then the reaction is said to occur "spontaneously" meaning that electrical current will be produced; it's a **electrochemical battery** or a **galvanic cell** or a **galvanic cell**.
3. If the cell's potential is negative, then the cell is an **electrolytic cell**, it is **electrolysis**, and electrical current will be needed. This is used for electroplating of one metal on another.
4. Note: in order to balance the electrons in a redox reaction, the reduction and oxidation reactions may need to be multiplied. However, this does not change the standard reduction potential. Why? Electric potential is energy per electron.

### 3.6 Galvanic Cell Example

Consider the following system which is to act as a galvanic cell (*i.e.*, spontaneously)

1. In the anode half-cell we have a solution of  $\text{ZnSO}_4$  and a zinc metal strip.
2. In the cathode half-cell we have a solution of  $\text{CuSO}_4$  and a copper metal strip.
3. The two metal strips are attached by a metal wire.

In the first half-cell we have the oxidation reaction (making it the anode)



In the second half-cell we have the reduction reaction (making it the cathode)



To find the cell potential we need to

- write the two reactions above as reduction reactions
- use the table in the textbook to find the standard reduction potentials
  - for the zinc half-cell (the anode)  $E^{\circ} = -0.76$  Volts
  - for the copper half-cell (the cathode)  $E^{\circ} = +0.34$  Volts

Notice how  $E$  for the copper is bigger than  $E$  for the zinc? Thus, copper wins the battle for the electrons and so must be the cathode.

- We need to subtract the  $E^{\circ}$  for the anode from the  $E^{\circ}$  for the cathode

$$E^{\circ} = (+0.34) - (-0.76) = 1.10 \text{ Volts}$$

### 3.7 Physical Description

Physically what is happening?

1. the solid Zn in the anode is dissolving into the solution forming  $\text{Zn}^{2+}$  and two electrons travel to the cathode
2. the solution of  $\text{Cu}^{2+}$  is plating out as solid copper on the cathode
3. the salt bridge is allowing the ions migrate between the half-cells to maintain the charge

The overall reaction is



### 3.8 Practice

For each of the following, use the table of standard cell potentials from your textbook (attached) to write the balanced redox reaction that would happen in a galvanic cell and give the cell potential.

1.  $\text{Ag(s)}$ ,  $\text{Cu(s)}$ ,  $\text{AgNO}_3(\text{aq})$ ,  $\text{Cu(NO}_3)_2(\text{aq})$
2.  $\text{Fe(s)}$ ,  $\text{Mg(s)}$ ,  $\text{Fe}^{2+}(\text{aq})$ ,  $\text{Mg}^{2+}(\text{aq})$
3.  $\text{Cd(s)}$ ,  $\text{Fe(s)}$ ,  $\text{Cd}^{2+}(\text{aq})$ ,  $\text{Fe}^{2+}(\text{aq})$
4.  $\text{Br}_2(\ell)$ ,  $\text{Cl}_2(\text{g})$ ,  $\text{Cl}^-(\text{aq})$ ,  $\text{Br}^-(\text{aq})$
5.  $\text{Ag(s)}$ ,  $\text{Pb(s)}$ ,  $\text{Ag}^+(\text{aq})$ ,  $\text{Pb}^{2+}(\text{aq})$