

Electrochemistry

Oxidation-Reduction reactions... (Review)

- Oxidation Numbers
The rules for assigning oxidation numbers can be found in Chapter 3 of your text.
- Oxidation vs. Reduction
Oxidation is a loss of electrons. Reduction is a gain of electrons.
- Balancing Oxidation Reduction Reactions
This is the “half-reaction” method of balancing oxidation-reduction reactions.

1. The initial “skeleton” reaction to be balanced for an oxidation-reduction reaction occurring in aqueous solution often does not include the H_2O , H^+ (in acid), or OH^- (in base) that will be added later as the reaction is balanced. Sometimes spectator ions are not included either. Write the skeleton reaction and assign oxidation numbers to each element.

2. Split the reaction into two half-reactions, one containing the oxidation and one containing the reduction. (Note: In some reactions, more than one element is oxidized or more than one is reduced. Sometimes the mole-to-mole relationships between these elements can be determined from the formulas of the chemicals involved in the reaction. However, in some cases, experimental data is needed to help determine the correctly balanced equation.)

3. For each half-reaction, balance of all the elements present **except** oxygen and hydrogen.

4. Balance oxygen by adding H_2O to the side of each half-reaction needing oxygen.

5. The method for balancing hydrogen in each half-reaction depends on whether the reaction is taking place in acidic or basic solution.

a. in acid, add H^+ to the side of the reaction needing more hydrogen.

b. in base, count the number of hydrogen atoms that are needed. Add one H_2O for every hydrogen needed to the side with insufficient hydrogen and simultaneously add the same number of OH^- ions to the opposite side

Note: # of H needed = # of H_2O added to the side with insufficient H = # of OH^- added to opposite side

6. Balance overall charge by adding electrons (e^-) to the more positive side of the half-reaction.
7. Multiply each half-reaction by the factors needed to make the electrons in each half-reaction equal.
8. Add the half-reactions (combining any like terms) and cancel species that appear on both sides of the equation (electrons must cancel).
9. If needed, divide by the largest common factor to reduce the coefficients to the lowest whole number ratio .
10. **CHECK** to make certain that the number of atoms of each element and overall charge are balanced.

Voltaic Cells

Named after Alessandro Volta who first developed a cell around 1800. Where would we be without this contribution from Alessandro Volta? Look around your house (in your mind) and see all of the items that utilize some sort of battery (or even just a single cell).

- watches
- calculators
- computers
- clocks (some types)
- remote controls

A **voltaic cell** is an electrochemical cell that generates an electric current through a spontaneous chemical reaction.

An **electrochemical cell** is a system consisting of electrodes dipped into an electrolyte solution and in which a chemical reaction either uses or generates an electric current.

The other type of electrochemical cell is called a **galvanic cell**. The galvanic cell uses electric current to drive a chemical reaction that would otherwise be nonspontaneous.

A voltaic cell consists of two **half-cells** that are electrically connected. Each half-cell is a part of an electrochemical cell where an oxidation-reduction half-reaction takes place.

The two half-cells are connected so that electrons can flow from one electrode to the other and ions can flow from one half-cell to the other. The two half-cells must be connected to allow ions to flow or the reactions will stop. The two electrodes cannot be in the same solution or the reaction will occur directly and no electric current will flow.

The half-cells are connected through a **salt bridge**. A salt bridge is a tube of electrolyte that allows ions to pass from one half-cell to the other without allowing the solutions to mix. A porous barrier can also be used such as in the alkaline cells used in personal electronics.

We have to have a way to distinguish between our electrodes. We can do this by examining what is happening at each electrode. The electrode at which reduction occurs is the **cathode**. The electrode at which oxidation occurs is the **anode**.

Which way do electrons flow in a voltaic cell?

Which way do the ions flow in a voltaic cell?

By examining the answers to these questions we can determine the signs on the electrodes in a voltaic cell. Because the cathode is where reduction occurs and reduction is a gain of electrons the electrons must flow into this electrode. This electrode is the **positive** electrode in a voltaic cell. Also, because the anode is where oxidation occurs and oxidation is a loss of electrons, the electrons must flow from this electrode. This electrode is the **negative** electrode in a voltaic cell.

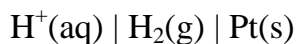
Cell Notation for Voltaic cells...

Example...

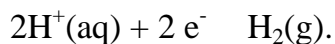


In this notation the anode (oxidation) is **always** written first (on the left) and the cathode (reduction) is always written last (on the right). The double parallel lines indicate the salt bridge. The cell terminals (electrodes) are at the extremes of the notation. In the above example one of the terminals (the anode) is solid zinc and the other (the cathode) is solid copper.

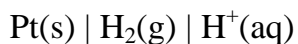
When a gas is involved in the half-reaction, an inert metal is the terminal and the surface on which the reaction takes place. An example of this is the hydrogen electrode (as a cathode):



where the half-reaction is:



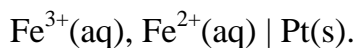
To write this as an anode we just reverse everything:



and the reaction is:

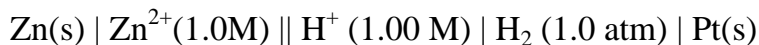


If there are two ions present in the same solution, they are separated by a comma in the notation:



The single vertical bar is used to separate different phases in the same cell. A comma is used to separate the same phase in the same cell.

To fully specify the cell, the conditions must be given. If they are not specified, they are assumed to be standard conditions (1 atm, 1 M). The conditions are specified in the cell like this:



Electromotive force...

Electrons, like everything else need some sort of reason to move. Air moves, causing winds because of differences in air pressure. Water moves due to differences in water pressure. Electrons move due to differences in electron pressure. This **electron pressure** is also known as the **potential difference**. The potential difference is the difference in potential between two points. This is measured in **volts**, which is the SI unit for potential difference. The work required moving the electrons, or the energy derived from the movement of electrons is equal to the produce of the charge on the electrons times the potential difference.

$$W_{\text{electrical}} = \text{charge} \times \text{potential difference}$$

where work is in Joules, charge is in coulombs and the potential difference is in volts.

The **Faraday constant** is the charge on 1 mole of electrons and has a value of 96,485 coulombs ($9.65 \times 10^4 \text{ C}$). The faraday is a unit of $9.65 \times 10^4 \text{ C mol}^{-1}$. The work done in moving this amount of charge is the product of the faraday constant and the potential difference. The work is the negative of this because the cell loses the energy to its surroundings.

$$w = -F \times \text{potential difference.}$$

In a normal cell the actual work is less than this because it requires some of the energy to drive the current through the cell itself. The cell has maximum voltage when **NO** current flows through the cell. We can measure this voltage with a voltmeter that draws a negligible amount of current from the cell.

The maximum potential difference between the electrodes of a voltaic cell is referred to as the **electromotive force (emf)** or E_{cell} . If n is the number of electrons transferred in the overall cell equation, then the maximum electrical work the cell can do is

$$w = -nFE_{\text{cell}}$$

Standard Cell emf's and Standard Electrode Potentials...

A cell has an emf based on the oxidation and the reduction that occurs in the cell. We can think of the cell emf as being a combination of the electrons being pushed by the oxidation and the electrons being pulled by the reduction. Each of which has a potential. So, the E_{cell} can be expressed as:

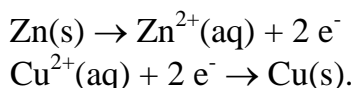
$$E_{\text{cell}} = \text{oxidation potential} + \text{reduction potential}.$$

The reduction potential can be thought of as a measure of the tendency of an oxidized species to gain electrons in the reduction half-reaction, or as a measure of its strength as an oxidizing agent. We can think of the oxidation as being the opposite of the reduction. Because the reaction has been reversed the oxidation potential has the opposite sign of the corresponding reduction potential. Therefore, we need only the reduction potentials or only the oxidation potentials. In practice, only the reduction potentials are tabulated.

For the zinc-copper cell we looked at earlier:



we have the following half-reactions:



The first of these is an oxidation. If we write E_{Zn} as the electrode potential for the **reduction** reaction then $-E_{\text{Zn}}$ is the potential for the oxidation reaction here. The copper reaction is a reduction so the potential is written as E_{Cu} . The emf is the sum of these two potentials:

$$E_{\text{cell}} = E_{\text{Cu}} + (-E_{\text{Zn}}) = E_{\text{Cu}} - E_{\text{Zn}}$$

Or in general terms

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{reduction}} + E_{\text{oxidation}}$$

The electrode potential is an **intensive property**, which means that its value does not depend on the amount of the species present. This means that if we have to multiply a reaction by a value to get the overall equation, we **DO NOT** multiply the potential by that same value.

Tabulated Standard Electrode Potentials

The potential of the cell however also depends on temperature and the concentrations (or pressures) of the substances present. The Standard cell potentials, E_{cell}° , however, are for certain specified conditions, usually 1 M

concentration and 1 atm pressure at 25 °C. The superscript (°) indicates that it is measured under standard conditions.

Only the cell emf can be measured. But if we had a table of electrode potentials we can calculate cell emf's from them. This is easier than tabulating cell emf's, because for as the number of possible electrodes grows the number of possible combinations grows exponentially.

If we want to know the potential of the electrode, though, we have to measure it against another electrode, which is our reference. The reference that is used is the Standard Hydrogen Electrode (S.H.E.) that is defined to have a potential of 0.00V. The Standard Electrode Potentials, E° , that are tabulated are all measured against S.H.E. They are all for the concentration of solutes as 1.00 M and pressures of gases as 1.00 atm at 25°C.

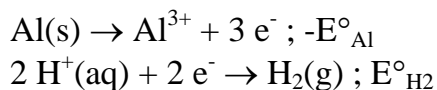
How do we get E° 's?

1. Connect the electrode we are trying to measure in a cell with S.H.E.
2. Measure the emf of the cell with a voltmeter. The electrode we are measuring should be the anode.
3. Write the cell notation for the cell.
4. Write the half reactions that correspond to the cell.
5. Express the cell emf as the sum of the half-cell potentials.
6. Do the math.

Let's look at an example. We place an aluminum electrode in a cell with the S.H.E. We measure the cell emf with a voltmeter and get 1.66 V with Aluminum as the anode. The cell notation for this cell is



The half-reactions, according to this are:



The cell emf is given by

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E^\circ_{\text{H}_2} - E^\circ_{\text{Al}} = 0.00\text{V} - E^\circ_{\text{Al}} = 1.66 \text{ V}$$

Which gives E°_{Al} as -1.66 V.

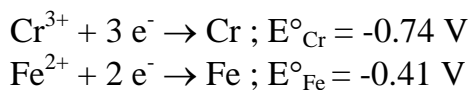
Strengths of oxidizing and reducing agents...

We can use the table of electrode potentials to determine the strengths of oxidizing and reducing agents. Because all of the potentials listed are for reductions we are looking at a table of oxidizing agents. In the table the oxidized species with half-reactions corresponding to the largest potentials are the strongest oxidizing agents. Conversely, the reduced species with half-reactions corresponding to the smallest potentials are the strongest reducing agents.

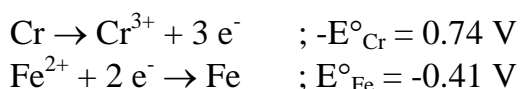
We can now use the table to predict the spontaneous direction of oxidation-reduction reactions. We just note their relative strengths. The stronger oxidizing agents will be on the reactant side in the spontaneous equation.

Calculating Cell emf's from standard potentials...

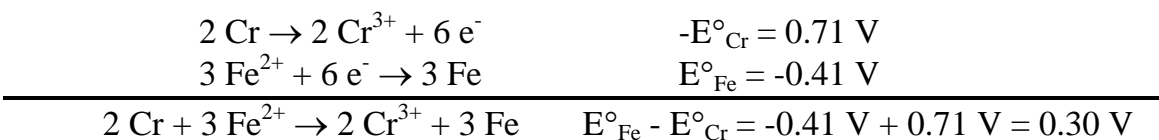
Let's look at a cell constructed from a Chromium/Chromium(III) electrode and an Iron/Iron(II) electrode. The half reactions and potentials are:



We need to reverse one of these reactions to get the oxidation part of the reaction, but which one. The half-reaction with the larger reduction potential stays the same. The half-reaction with the smaller reduction potential gets reversed. In this case we are left with



We get the cell reaction by adding the two reactions remembering to balance out the electrons.



The cell emf is 0.30 V and the cell diagram is



Equilibrium constants from emf's...

If we remember that the change in Gibb's free energy is the same as the maximum amount of work that can be obtained from a process. We can determine the ΔG for a voltaic cell.

$$\Delta G = w_{\max}$$

$$w_{\max} = -nFE^{\circ}_{\text{cell}}$$

Therefore,

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

Now we can use cell emf's to calculate thermodynamic data or vice-versa.

A cell is composed of the Cr/Cr³⁺ electrode and the Fe/Fe²⁺ electrode. What is the free energy change for the cell? What is the equilibrium constant for the cell?

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

We calculated earlier that E°_{cell} is 0.30V. We found that in the cell equation 6 moles of electrons are transferred. Plugging these values into the equation gives:

$$\begin{aligned}\Delta G^{\circ} &= - (6 \text{ mole } e^{-}) (9.65 \times 10^4 \text{ C/mol } e^{-}) (0.30 \text{ V}) \\ &= -173700 \text{ J} = -1.7 \times 10^2 \text{ kJ}\end{aligned}$$

We can calculate the equilibrium constant from either the cell potential or the Free energy change of the cell. Here, we will use the cell potential.

$$K = e^{-\frac{\Delta G^{\circ}}{RT}} = e^{-\frac{nFE^{\circ}_{\text{cell}}}{RT}} = e^{-\frac{(6)(9.65 \times 10^4)(0.30)}{(8.314)(237.15)}} = e^{76.487} = 1.65 \times 10^{33}$$

For a fuel cell:



What is the cell emf?

How many electrons are transferred in the reaction? Hydrogen changes its oxidation state from 0 to +1 for a loss of 1 electron per hydrogen atom. There are 4 hydrogen atoms so 4 electrons are transferred in the reaction.

$$\Delta G^\circ = -nFE^\circ_{\text{Cell}}$$

$$E^\circ_{\text{cell}} = -\Delta G^\circ/nF = -(-474.4 \text{ kJ}) / (4 \text{ mol } e^-) (96500 \text{ C/mol } e^-) \\ = 1.229015544041 \text{ V} = 1.23 \text{ V}.$$

Dependence of emf on concentration...

If we remember that the free energy of a reaction is dependent on the concentration of the reactants:

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

and that the free energy is related to the cell emf:

$$\Delta G = -nF\Delta E^\circ$$

we arrive at the relationship between cell emf and concentration:

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

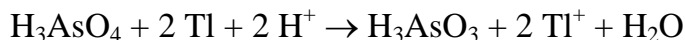
At room temperature (25°C, 298 K) this breaks down to

$$\Delta E = \Delta E^\circ - \frac{RT}{nF} \ln Q = \Delta E^\circ - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(273.15 \text{ K})}{n(96485 \text{ C mol}^{-1})} \ln Q \\ = \Delta E^\circ - \frac{0.02569}{n} \ln Q$$

If we look at this equation we realize that the cell emf decreases as the reaction proceeds. The concentrations of the products decrease and the concentrations of the reactants increase. This causes Q to increase and ln Q to increase.

Q: What is the cell emf of a cell comprised of Tl^+/Tl half-cell ($E^\circ = -0.336 \text{ V}$) and a $\text{H}_3\text{AsO}_4(\text{aq})/\text{H}_3\text{AsO}_3(\text{aq})$ (Pt electrode) half-cell ($E^\circ = +0.575 \text{ V}$) if the concentration of Tl^+ is 0.100 M, of Arsenic acid is 0.250 M, the pH is 8.64 and Arsenous acid is 0.110 M?

A: Because the thallium half-cell has the lower reduction potential, it is the anode. This give a balance chemical equation of:



$E^\circ_{\text{cell}} = 0.911 \text{ V} - (-0.336 \text{ V})$ and there are 2 electrons transferred per reaction unit. The cell emf will be:

$$\begin{aligned} \Delta E &= \Delta E^\circ - \frac{RT}{nF} \ln Q = 0.911 \text{ V} - \frac{(8.314 \frac{\text{J}}{\text{mol K}})(298.15 \text{ K})}{(2 \frac{\text{mol e}^-}{\text{mol}})(96485 \frac{\text{C}}{\text{mol e}^-})} \ln \frac{[\text{I}^-]^2 [\text{H}_2\text{AsO}_3]}{[\text{H}_3\text{AsO}_4][\text{H}^+]^2} \\ &= 0.911 \text{ V} - 0.01285 \text{ V} \cdot \ln 2.776 \times 10^{-20} = 1.490 \text{ V} \end{aligned}$$

This example shows that the cell emf can be increased or decreased by adjusting the reactants in the appropriate way.

This also has applications as a pH electrode:



This cell has a STANDARD potential of 0.76 V. If we measure the cell emf for a solution that is not 1 M H^+ we can calculate the pH of the solution.

$$\Delta E = \Delta E^\circ - 0.02569/2 \log (1/[\text{H}^+]^2)$$

rearranging gives

$$\text{pH} = (0.76 - \Delta E) / 0.02569$$

We can also use voltaic cells to obtain equilibrium constants. When the cell is at equilibrium the cell no longer puts out any voltage ($E=0$). Also at equilibrium the reaction quotient is equal to the equilibrium constant ($Q=K$). The relationship between standard cell potential and the equilibrium constant can then be obtained:

$$\begin{aligned} \Delta E &= \Delta E^\circ - \frac{RT}{nF} \ln Q \\ 0 &= \Delta E^\circ - \frac{RT}{nF} \ln K \\ \ln K &= \frac{nF \Delta E^\circ}{RT} \end{aligned}$$

This relationship always holds. We can use it to calculate the equilibrium constant of a reaction if we know the standard potential of the reaction. For most reactions of voltaic cells the equilibrium constant will have a very large value ($K \gg \gg 1$). For

extremely large values of K, significant figures really no longer have any meaning and the K is simply reported as some power of 10.

Electrolytic cells

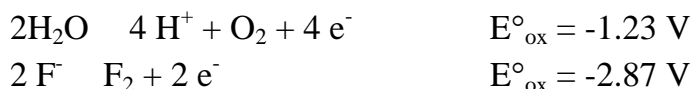
Just as we can use a spontaneous reaction to produce an electrical current, we can use an electrical current to drive a non-spontaneous reaction. The cell in which this occurs is called an **electrolytic cell**. Electrolytic cells have a variety of uses. They can be used to separate Hydrogen and Oxygen in water, obtain pure elements from their compounds and electroplating. The voltages for electrolytic cells are always negative (energy must be supplied).

Electrolysis of aqueous salts

When a solution containing an aqueous salt is placed in an electrolytic cell there are at least two possibilities for what can happen at each electrode. Suppose we have a solution of Sodium Fluoride in water. If we electrolyze the solution we can predict what will happen at each electrode. At the cathode (reduction) we have two possibilities:



The reaction more likely to happen is the one with the more positive reduction potential ($\text{H}_2\text{O} \rightarrow \text{H}_2$). At the anode (oxidation) there are also two possibilities:



Again the more likely to occur is the one with the more positive **oxidation** potential ($\text{H}_2\text{O} \rightarrow \text{O}_2$). So in this cell we would expect to see Hydrogen gas produced at the cathode and Oxygen gas produced at the anode.

Electroplating

An electrolytic cell can also be used to plate metals onto a surface. This is done in a cell that contains an electrolyte that contains the metal to be plated (e.g., Cr^{3+}). The object to be plated acts as one of the electrodes. A piece of the metal to be plated acts as the other electrode. The current is supplied to the cell and causes the metal ions in solution to gain electrons and plate out onto the object. The rate at which the metal is plated depends only on the mass to be plated and the current

supplied, more current, less time. Current is measured in **amperes**. One ampere is equivalent to one coulomb per second. Therefore, if we know how much current is supplied and the mass of metal to be plated we can calculate how long it will take and vice versa.

A bracelet with a surface area of 6.0 cm^2 is to be plated with silver to a thickness of 0.025 cm . If the current supplied to the cell is 8.75 amps , how many hours will it take to plate the bracelet?

The volume of silver to be plated is:

$$6.0 \text{ cm}^2 \times 0.025 \text{ cm} = 0.15 \text{ cm}^3$$

The density of silver is 10.3 g cm^{-3} . The time can be calculated as:

$$0.15 \text{ cm}^3 \times \frac{10.3 \text{ g}}{\text{cm}^3} \times \frac{1 \text{ mol Ag}}{107.8682 \text{ g}} \times \frac{1 \text{ mol e}^-}{1 \text{ mol Ag}} \times \frac{96485 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{8.75 \text{ C}} \times \frac{1 \text{ hr}}{3600 \text{ s}} = 0.044 \text{ hours}$$