

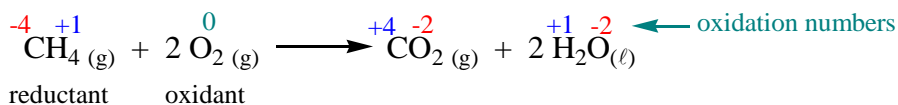
## Chapter 17 – Electrochemistry

We will now examine, in depth, reactions in which electrons are passed from one species to another. These reactions were first introduced in Section 4.2 and involve changes in oxidation numbers. In particular, you should go back now and review how to assign oxidation numbers. Much of the work in this chapter requires you to do this.

Reactions involving a change in oxidation numbers of two or more substances are called oxidation-reduction reactions. They are also called redox or electron transfer reactions. In general, the study of reactions involving the movement of electrons is called electrochemistry.

### 17.1 Review of Redox Chemistry

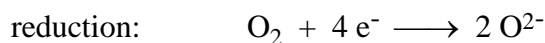
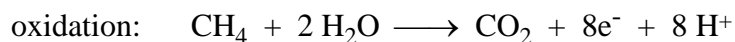
In a redox reaction both an oxidation and a reduction must occur. After all, the gained (or lost) electron must come from (or go to) somewhere. The substance that loses electrons is called the reducing agent or reductant. It is oxidized. The species gaining electrons is called the oxidizing agent or oxidant. It is reduced.



There are a few things worth remembering about redox reactions. Again, **oxidation and reduction must both occur in a redox reaction**. The second ties into the previous observation. One must be careful when using oxidation states. In some cases, the oxidation number of a species represents the actual charge on a species (e.g. -1 on chloride in sodium chloride), in others it does not (e.g. -1 on Cl in CCl<sub>4</sub>). The difference is that, in the former case we have an ion, while in the latter chlorine is in a molecule. **In general, do not assume the oxidation number on an atom is the same as the actual charge on the atom.**

## Balancing Redox Equations

For all redox reactions, the oxidation and reduction steps can be extracted into separate equations explicitly showing the movement of electrons. These are called half-reactions. For the previous example:



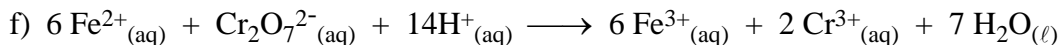
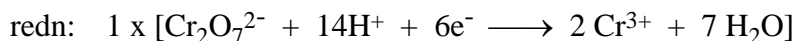
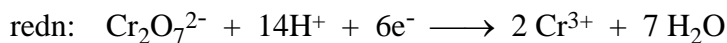
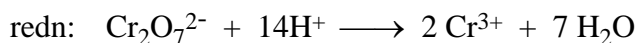
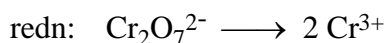
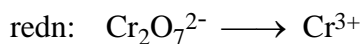
The oxidation half of this pair looks a little involved, but you'll see shortly how it comes about. There is a set of rules that, if followed exactly, always yields balanced redox reactions. In the stoichiometry chapter, you balanced some redox reactions by inspection or by the method shown in the text. This will work for some redox reactions with relative ease, however, others will be very, very difficult to solve using these methods. For that reason, if you can't balance very quickly using the other methods, use this one. For the purpose of practice, you should use only this method in this chapter, or else you won't become adept enough to use it when you have to.

### Method of Half-Reactions

- 1) Divide the unbalanced overall reaction into the oxidation and reduction parts (you'll need the oxidation numbers to do this).
- 2) Balance the elements other than H and O by any method.
- 3) Balance H and O by adding  $\text{H}^+$  and  $\text{H}_2\text{O}$ , respectively, if necessary.
- 4) Balance the charge by adding electrons.
- 5) Multiply the coefficients of each half-reaction by the smallest factor such that the number of electrons consumed in the reduction equals the number of electrons produced in the oxidation.
- 6) Add the half-reactions and simplify.
- 7) If the reaction was done in basic solution, add enough  $\text{OH}^-$  to each side to exactly react with

the  $\text{H}^+$  in the balanced equation. (This can also be done after step 4 or at the very end, whichever you prefer.)

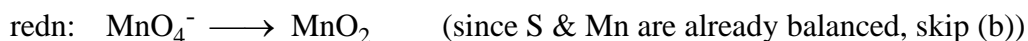
Ex: Balance the reaction:  $\text{Fe}^{2+}_{(\text{aq})} + \text{Cr}_2\text{O}_7^{2-}_{(\text{aq})} \longrightarrow \text{Fe}^{3+}_{(\text{aq})} + \text{Cr}^{3+}_{(\text{aq})}$  (acidic solution)

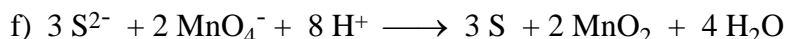
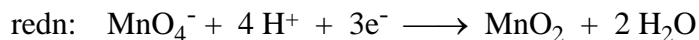
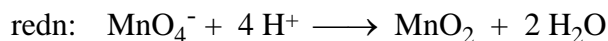


At this point you should check to make sure that the element totals are the same on both sides and that the total charge on each side is the same. (This is very important. If this wasn't necessary, part (a) oxidation would already be balanced. Yet the two species are clearly not identical.)

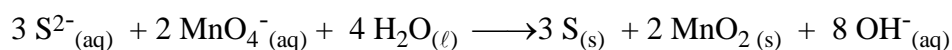
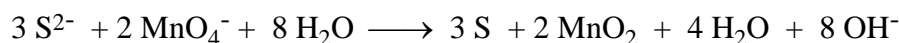
To balance reactions in basic solution, initially balance it just like an acidic reaction. At the end there will be an additional "step g" that will convert the reaction from acidic to basic solution.

Ex: Balance:  $\text{S}^{2-}_{(\text{aq})} + \text{MnO}_4^- \longrightarrow \text{S}_{(\text{s})} + \text{MnO}_2_{(\text{s})}$





g) Now add 8 OH<sup>-</sup> to each side. The OH<sup>-</sup> will react with H<sup>+</sup> to yield water.

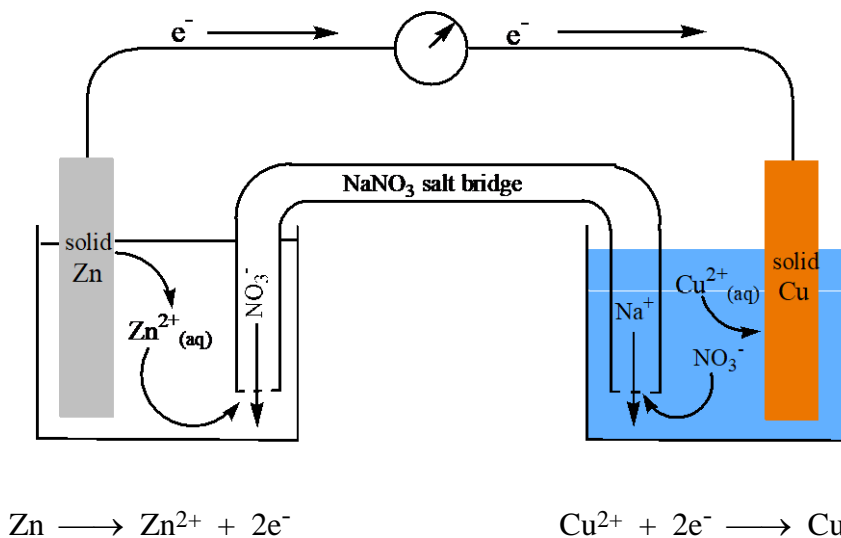


## 17.2 Galvanic Cells

The electrons that flow in redox reactions can do work. The most common device for harnessing this energy is the battery (see Section 17.5).

Batteries are a type of voltaic or galvanic cell. These are devices that require the electrons to move along an external pathway, instead of directly between reacting species. In normal reactions, the reactants are mixed in the same container (they couldn't react if they weren't). In redox reactions, the reactants can actually be placed in separate containers that are connected such that electrons can flow between them.

Consider the reaction  $\text{Cu}^{2+}_{(\text{aq})} + \text{Zn}_{(\text{s})} \longrightarrow \text{Cu}_{(\text{s})} + \text{Zn}^{2+}_{(\text{aq})}$ . The figure below shows a fairly typical voltaic cell.



Devices inserted into solution to act as sites of electron exchange are called electrodes. In the picture above, the solid zinc and copper blocks are electrodes. It is important to remember that electrodes need not be made of the same material as the species undergoing redox processes. In fact, the most common substances used for electrodes are platinum and graphite. These are inert electrodes, so called because they simply provide a platform for electron transfer. The electrodes in the picture are called active electrodes because they chemically participate in the reaction. The electrode at which oxidation occurs is called the anode, while reduction occurs at the cathode. In the picture, the zinc strip is the anode, while the copper piece is the cathode. The anode is labeled with a negative charge, the cathode with a positive charge. Why? When oxidation occurs, electrons are left on this electrode. They then flow towards the cathode which is labeled positive because if negatively charged electrons move in that direction, it must be positive relative to the anode.

For current to flow there must also be a salt bridge between the vessels. This is because when  $\text{Zn}^{2+}$  forms there must be a counterion present as well. Likewise, when  $\text{Cu}^{2+}$  reduces to copper metal, there will be an excess of nitrate ions. The salt bridges keep each reaction container

electronically neutral by removing or adding ions as appropriate.

Cell Notation – Read on your own.

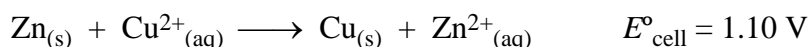
### 17.3 Electrode and Cell Potentials

In redox reactions electrons move because, as in all reactions, the products are more stable than the reactants. We could use  $\Delta G$ , but that must be calculated. It would be far easier to use a directly measurable quantity.

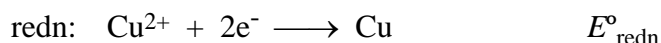
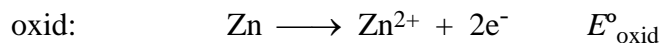
The volt (V) measures the potential energy difference between the electrodes. One volt is the potential difference imparting one joule of energy to a one coulomb (C) charge. The electromotive force (emf) is the potential difference between two electrodes in an electrochemical cell. It is also frequently called the cell potential,  $E_{\text{cell}}$ . When reactions are done under standard state conditions (1 atm, 1 M, 25 °C), one obtains a standard emf or standard cell potential,  $E^{\circ}_{\text{cell}}$ .

$$1 \text{ V} = \frac{1 \text{ J}}{\text{C}}$$

For the cell in the picture on the previous page, the emf is measured as:

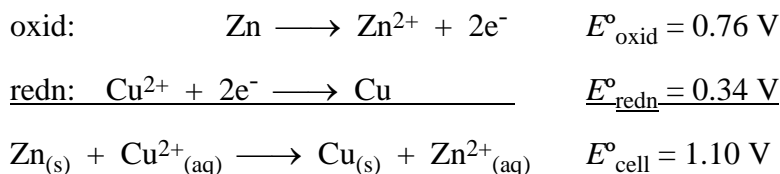


But this reaction is just the sum of two half-reactions. The following discussion is different from the textbook, but I find it easier to understand. The two half-reactions for this cell are shown below:



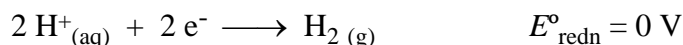
Since the reduction looks just like the half-reaction in the reduction potentials table (Table 17.1 and Appendix L) we copy the number down exactly. The oxidation is reversed from the table

( $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$ ,  $E^\circ_{\text{redn}} = -0.76 \text{ V}$ ) and, in this case, we change the sign on the value from the tables. Now we can add the half reactions to get the net reaction and add the oxidation and reduction half-cell potentials to get the overall cell potential.



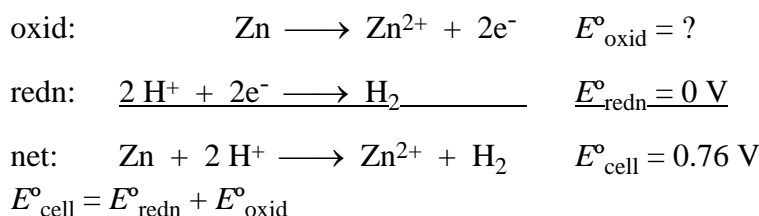
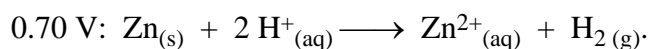
Thus:  $E^\circ_{\text{cell}} = E^\circ_{\text{redn}} + E^\circ_{\text{oxid}}$  (if you write the half-cells as above). **Note:** The book uses a very similar equation  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ , which differs from the equation I use in that it draws its values straight from the *Reduction Potential Table* (17.1), while the formula I present puts the values in association with the reactions as they actually occur.

Earlier we said that oxidations and reductions cannot happen independently of one another, so how can we measure half-cell potentials? Actually, we can't. Using half-reactions requires us to define the potential of one reaction, then measure all others relative to it. This is a lot like how  $\Delta H$  is treated. The reaction used to define emfs is:



Thus, whenever the hydrogen electrode is used, the cell potential equals the potential for the other half-reaction (or its reverse, depending on the direction of the hydrogen reaction).

Ex. Find the reduction potential for the oxidation of zinc, if the emf for the following reaction is



$$0.76 \text{ V} = 0 + E^{\circ}_{\text{oxid}}$$

$$E^{\circ}_{\text{oxid}} = 0.76 \text{ V}$$

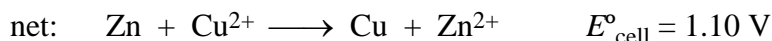
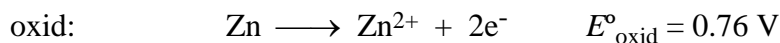
But we want the reduction potential of zinc (the reverse of the reaction show above, so we need to change the sign on our answer.



This is generally true, [when a half-reaction is reversed, the sign on emf changes](#).

Ex. What is  $E^{\circ}_{\text{cell}}$  for the reaction:  $\text{Zn}_{(\text{s})} + \text{Cu}^{2+}_{(\text{aq})} \longrightarrow \text{Cu}_{(\text{s})} + \text{Zn}^{2+}_{(\text{aq})}$  using the values in

17.1 on pp. 907-909?



An important feature of electrochemistry is that [cell potential doesn't depend on reaction stoichiometry](#). Is this reasonable? Consider the reaction  $3 \text{Cu}^{2+} + 2 \text{Al} \rightarrow 3 \text{Cu} + 2 \text{Al}^{3+}$ . The function of the extra copper ions is simply to take away more electrons. The energy of the copper hasn't changed.

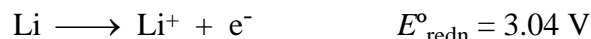
Open your book to Table 17.1 before going further. This is a list of standard reduction potentials. The first reaction, the reduction of fluorine to fluoride, is one that you would expect to proceed spontaneously. It has a positive  $E^{\circ}_{\text{redn}}$  and this can be a convenient way to remember



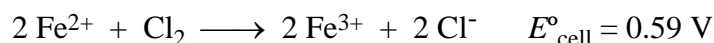
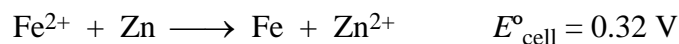
the sign for spontaneity when you look at a reduction potential table. Remember that any reaction spontaneous in one direction is nonspontaneous in the other. Thus, at the other end of the table, the reduction of lithium ions to lithium metal is very unfavorable (very negative). Hence, [any](#)



reaction on the table coupled with a reaction below it run backwards will yield a



spontaneous net reaction. It is also important to note that the same species can act as a reductant in one reaction and an oxidant in another. For example:



Finally, the more positive a reduction potential, the better oxidant the species is. Conversely, the more negative a reduction potential, the better the species to the right of the arrow (in a half-reaction) is as a reductant.

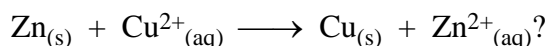
#### 17.4 Potential, Free Energy, and Equilibrium

It is important to remember that any reaction with a positive  $E^{\circ}$  value is spontaneous. We know from Chapter 16 that reactions are spontaneous when  $\Delta G^{\circ}$  is negative. Therefore, the two must be mathematically related. The equation that accomplishes this is:

$$\Delta G^{\circ} = -nFE^{\circ}$$

where “n” is the number of moles of electrons transferred and  $F$  = Faraday constant = 96,500 C/mol = 96,500 J/V•mol.

Ex. What is the standard free energy change for the reaction



$$\Delta G^{\circ} = -(2 \text{ mol}) \left( \frac{96,500 \text{ J}}{\text{V} \cdot \text{mol}} \right) (1.10 \text{ V}) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) = -193 \text{ kJ}$$

Equilibrium constants may also be calculated from cell potentials using the equations:

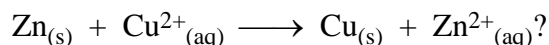
$$\Delta G^{\circ} = -RT \ln K_{\text{eq}} \quad \text{and} \quad \Delta G^{\circ} = -nFE^{\circ}$$

combine to yield

$$-nFE^\circ = -RT\ln K_{\text{eq}}$$

$$E^\circ = \frac{RT}{nF} \ln K_{\text{eq}}$$

Ex. What is the equilibrium constant for the reaction



$$1.10 \text{ V} = - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(96,500 \text{ J/V} \cdot \text{mol})(2 \text{ mol})} \ln K_{\text{eq}}$$

$$\ln K_{\text{eq}} = 85.7$$

$$K_{\text{eq}} = 1.64 \times 10^{37}$$

Of course, this is hardly an equilibrium in the real sense of the word. (Indeed, to have a single  $\text{Cu}^{2+}$  ion left in the solution after adding zinc to a 1 M  $\text{Cu}^{2+}$  solution, the container size would have to be around 27 trillion liters (a cube 1.86 miles on a side).) For a reaction with one electron transferred and a  $E^\circ = 0.10 \text{ V}$  the equilibrium constant would be around 50, for 0.20 V it is 2400. As you can see equilibrium constants increase quite rapidly with cell potential. Thus, this equation is of limited value.

### Potentials at Nonstandard Conditions: The Nernst Equation

Functionally, cells are never at standard conditions. That is, the vast majority of the time, they aren't constructed at standard conditions and even when they are, as soon as you start using them the conditions shift away from standard conditions. (i.e. If everything is at 1 M concentration, as soon as current begins to flow, the concentration will change. There is no practical way to maintain the concentrations of everything at 1 M throughout an experiment.)

The Nernst equation compensates for non-equilibrium conditions in electrochemical reactions. The equation is related to the non-equilibrium conditions reaction at the end of Chapter

16:  $\Delta G = \Delta G^\circ + RT\ln Q$ .

For electrochemical systems the comparable equation is:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$

If the temperature is 25 °C and the logarithm is changed to base-10, the equation simplifies to

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \ln Q$$

Generally speaking, while electrochemical experiments set-up under non-standard state will cause shifts to the cell potential, those shifts will not be large enough to alter the determination of spontaneity made under standard state conditions. The book's example 17.7 (pp. 913-14) illustrates this point nicely. The provided reaction  $\text{Co}_{(s)} + \text{Fe}^{2+}_{(aq)} \rightarrow \text{Co}^{2+}_{(aq)} + \text{Fe}_{(s)}$  is non-spontaneous under standard conditions ( $[\text{Fe}^{2+}] = [\text{Co}^{2+}] = 1.0 \text{ M}$ ). Changing the concentrations so that  $[\text{Fe}^{2+}] \approx 13 \times [\text{Co}^{2+}]$  doesn't change the spontaneity. Looking at the math, it's clear that when the differential gets a bit higher that the spontaneity will change, but for most small changes to conditions for most reactions, there won't be a change to spontaneity.

Feel free to read the text on concentrations cells, which are conceptually both very interesting and weird, but you aren't responsible for this material.

## 20.7 Batteries and Fuel Cells

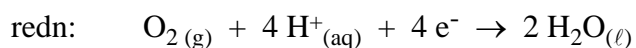
This section discusses four types of voltaic cells that have practical uses. The first three are batteries that you may well be familiar with: the dry cell/alkaline battery, rechargeable batteries, and the lead acid (car) battery. The final entry is for fuel cells, which are not currently commercially very important today, but will become so in the reasonably near future. They have the advantage of providing large amounts of electricity with no direct pollution and refueling will be far simpler than recharging a battery. [Large ship manufacturers are looking to fuel cells as a](#)

[way of powering cargo ships.](#) [Land vehicle manufacturers are also exploring fuel cells as a way of powering trucks and, possibly, cars in the future.](#) Read this section on your own.

## 17.6 Corrosion

Corrosion is the electrochemical breakdown of metals by the environment. It is nearly always oxygen oxidation, which is thermodynamically favorable for most metals under ambient conditions. Only gold will not corrode for thermodynamic reasons. Other factors prevent platinum and palladium from corroding. All other metals corrode, although the apparent rates vary significantly. Corrosion may either be very destructive, as in the cases of iron and zinc, or hardly noticeable, as for aluminum or chromium. The reason for the variation results from the nature of the products. In all cases, a metal oxide results from air oxidation of the metal. Aluminum oxide,  $\text{Al}_2\text{O}_3$ , adheres strongly to aluminum metal and thus provides a protective coating on the metal. Further oxidation does not occur because neither oxygen nor water (*vide infra*) can penetrate it. In contrast, when destructive oxidation occurs, the metal oxide flakes off. This constantly provides fresh metal for further oxidation until, finally, all of the metal oxidizes.

Interestingly, while corrosion certainly requires oxygen, acidic water is also a requirement. The more acidic the water, the faster corrosion occurs. The half-reactions for this process follow:



One reason corrosion is such a problem is that not all of the metal need be exposed to the environment. In “normal” reactions, the reactants must collide with each other (or intermediates) for the reaction to occur. Since metals conduct electricity, exposure of relatively small areas of the metal can cause significant corrosion.

There are several ways to prevent corrosion. A common way is to seal the surface with paint or plastic so that air and water don't have access to the metal. This works unless the paint chips or peels off. The other common method is to either coat the surface with a metal that is easier to oxidize (galvanization) or to attach the metal by wire to a block of easier to oxidize metal located elsewhere. For example, iron is usually protected with either zinc or magnesium. In these cases, the second metal is sacrificed.

Note the magnesium and zinc are not chosen because they are less expensive than iron. In fact, they cost more per pound. The philosophy for doing this goes as follows. The manufacturer of a product containing sheet metal can't know where the paint will be scratched or flake off. A thin coat of zinc over the whole sheet will protect against a scratch anywhere because of the ability of the metal sheet to conduct electricity. The zinc coating costs very little and will protect the sheet (until the scratch is painted over) from rust that could eat all the way through the sheet. If nothing is done, the scratch will result in rust going all the way through a panel and requiring its replacement. This is much more expensive than the cost of the coating. The same sort of logic governs using zinc or magnesium blocks to protect pipes or bridges.

### 17.7 Electrolysis

All of the reactions discussed in this chapter to this point occur naturally (spontaneously) in the forward direction. They are nonspontaneous in the reverse direction. Electrochemical reactions can be pushed in the nonspontaneous direction by providing an external current source. A processes driven by an external source of electrical energy is called electrolysis.

In an electrolytic cell, electrodes are placed into either molten salt or a solution of the ions to be electrolyzed. A current is then passed through the solution with a potential that is larger than

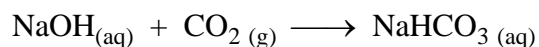
the  $E^\circ_{\text{rxn}}$  for the formation of the material. This drives the reaction in reverse.

The book has a nice picture of how molten table salt, NaCl, is electrolyzed to yield elemental sodium metal and chlorine gas on p. 926, Figure 17.18.

An interesting thing may happen when a salt is electrolyzed in aqueous solution. It is easier to reduce water than many metal ions. When this happens, the metal ion remains unchanged and water is reduced to hydrogen gas and hydroxide ion.



This is how commercial sodium hydroxide (caustic soda) is made. It is one of the highest volume chemicals produced in the world today. If carbon dioxide is bubbled through the solution, sodium bicarbonate, NaHCO<sub>3</sub>, forms.



### Quantitative Aspects of Electrolysis

There is great practical interest in how much electricity is required to perform an electrolysis experiment. At the industrial scale, the price of electricity will be a significant factor in the cost of the process and at both large and small scales the rate of delivery of the electrons will affect the speed at which the reaction proceeds. For example, all aluminum is produced by electrolysis. For that reason, aluminum manufacturers typically locate their foundries near inexpensive sources of electricity (e.g. the Pacific northwest because of that location's hydroelectric dams).

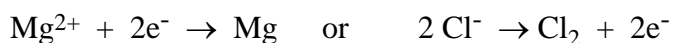
The amount of energy associated with an electrochemical process depends on the total number of electrons that flow between the electrodes. (After all, electricity is just the flow of electrons.) Since the charge on the electron is fixed, we can measure the flow of electrons by monitoring the charge as it passes by a fixed point. The rate of charge movement is measured in terms of amperes, A, where

$$1 \text{ A} = 1 \frac{\text{C}}{\text{s}}$$

Recall that the coulomb a measure of charge where 1 mole of electrons carries 96,500 C (or 1  $\mathcal{F}$ ) of charge. Thus, we can calculate either the amount of electricity produced by a redox reaction or the amount required to effect an electrolysis.

Ex. How much magnesium and chlorine are produced when a current of 0.452 A is passed through molten magnesium chloride for 1.50 hours?

First generate a balanced half-reaction for either element.



For each element it is important to balance using whole number coefficients.

This is a relatively complicated dimensional analysis problem. You can begin with either the given electrochemical data or the molecular weight of the element. Both methods are used below.

$$\begin{aligned} \text{mass}_{\text{Mg}} &= (0.452 \text{ A}) \left( \frac{1 \text{ C}}{\text{A} \cdot \text{s}} \right) \left( \frac{3600 \text{ s}}{\text{hr}} \right) (1.50 \text{ hr}) \left( \frac{1 \mathcal{F}}{96,500 \text{ C}} \right) \left( \frac{1 \text{ mol}_{\text{Mg}}}{2 \mathcal{F}} \right) \left( \frac{24.31 \text{ g}_{\text{Mg}}}{\text{mol}_{\text{Mg}}} \right) \\ &= 0.307 \text{ g}_{\text{Mg}} \end{aligned}$$

$$\begin{aligned} \text{mass}_{\text{Cl}_2} &= \left( \frac{70.90 \text{ g}_{\text{Cl}_2}}{\text{mol}_{\text{Cl}_2}} \right) \left( \frac{1 \text{ mol}_{\text{Cl}_2}}{2 \mathcal{F}} \right) \left( \frac{1 \mathcal{F}}{96,500 \text{ C}} \right) \left( \frac{1 \text{ C}}{\text{A} \cdot \text{s}} \right) \left( \frac{3600 \text{ s}}{\text{hr}} \right) (1.50 \text{ hr})(0.452 \text{ A}) \\ &= 0.897 \text{ g}_{\text{Cl}_2} \end{aligned}$$

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