

## Chapter 65

## ECHEM, Part 5

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This last Chapter on our echem coverage is a bit of a mix. First, we discuss the electrolytic cell. Then, we return to current and we consider electrochemical calculations which deal with current and with stoichiometry using electrons. After that, we discuss a different side of echem.

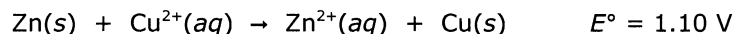
## 65.1 More electrolytic

There has been little discussion so far on electrolytic applications, and most of that has been for recharging batteries. There's actually much more to electrolysis in general. Keep in mind that the defining difference between galvanic and electrolytic cells is in the sign of  $\Delta G$  and therefore of  $E$ .

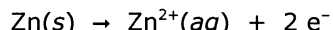
Galvanic cells have negative  $\Delta G$  and positive  $E$ .  
Electrolytic cells have positive  $\Delta G$  and negative  $E$ .

In a galvanic process, the overall chemical energy of the system decreases, and that provides the electrical energy which comes out of the cell. In an electrolytic process, electrical energy is put into the cell in order to increase the overall chemical energy of the system. Let's compare the two, using the Zn + Cu<sup>2+</sup> galvanic cell which we've been discussing quite a bit since Chapter 62.

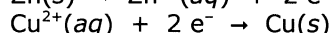
The galvanic process is given by the following.



Oxidation (anode)



Reduction (cathode)


**GALVANIC**

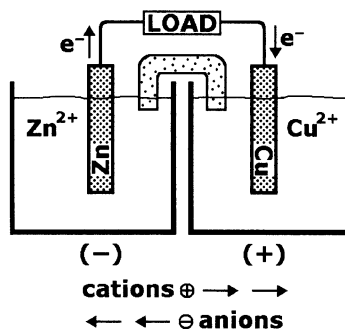
OXIDATION HALF-REACTION

Zn is the anode.

This is the anode compartment.

Electrons leave this half-cell, so this is the electrical negative side.

The direction of ion flow is:



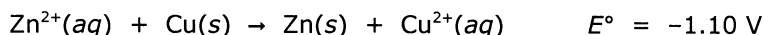
REDUCTION HALF-REACTION

Cu is the cathode.

This is the cathode compartment.

Electrons enter this half-cell, so this is the electrical positive side.

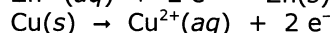
Now reverse the process and turn it into an electrolytic cell. Connect it to a battery (or other DC power source) of suitable voltage. The electrolytic process is given by the following.



Reduction (cathode)



Oxidation (anode)


**ELECTROLYTIC**

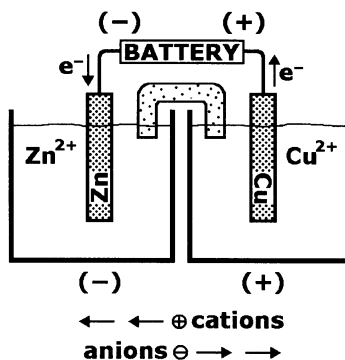
REDUCTION HALF-REACTION

Zn is the cathode.

This is the cathode compartment.

Electrons exit the battery (-) end to enter this half-cell, so this is the electrical negative side.

The direction of ion flow is:



OXIDATION HALF-REACTION

Cu is the anode.

This is the anode compartment.

Electrons enter the battery (+) end from this half-cell, so this is the electrical positive side.

Keep in mind that  $E^\circ$  and  $\Delta G^\circ$  are related by a negative sign. A cell with a positive  $E^\circ$  (negative  $\Delta G^\circ$ ) can apply a voltage to a load whereas a cell with a negative  $E^\circ$  (positive  $\Delta G^\circ$ ) must have a voltage applied to the cell. Sign is direction, but direction can also be specified in wording. For the present electrolytic example, we can write  $E^\circ = -1.10$  V or we can say the battery applies 1.10 V (without the minus sign) to the cell.

Here are several important considerations in comparing the above galvanic and electrolytic applications.

The values of  $E^\circ$  are the same in magnitude but opposite in sign.

The half-cells switch their roles as anode and cathode.

The current flow is in the opposite direction. This includes the electrons in the external circuit and the ions through the salt bridge.

Although the current is going in opposite directions and the anode/cathode character of the half-cells have switched, the electrical polarity signs (the +/- poles) for each half-cell stay the same. The electron flow is still from anode to cathode.

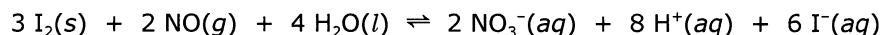
The  $\Delta G^\circ$  of the chemical reaction provides the drive for the galvanic direction. The external battery provides the drive for the electrolytic direction. If the battery is wired as shown in the electrolytic diagram above, and if its voltage is 1.10 V, then that matches (but opposes) the drive provided by  $\Delta G^\circ$ . As such, no current flows, there is no net change, and the system is in "electrochemical balance". In order for an electrolytic process to actually occur, the battery voltage must overmatch the potential of the galvanic process.

Note that "electrochemical balance" simply represents electrical balance. It is not the same as chemical equilibrium, which is a point of balance defined by  $K$  or by  $\Delta G = 0$  or by  $E = 0$ .

By the way, although the above picture shows a salt bridge, that will not allow sufficient current flow in a typical application, so operational cells will incorporate more sophisticated methods for separating the half-cell solutions.

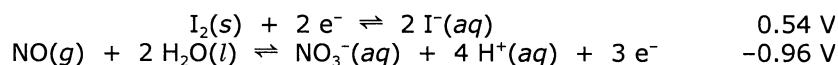
On a fundamental level, many of the prior calculations as done for galvanic cells can be done analogously for electrolytic cells. One important point is that, when working with equations for two half-reactions from Appendix C at standard conditions, you will now reverse the half-reaction which is higher on the list while the lower half-reaction will stay written as a reduction. That will guarantee that the  $E^\circ$  of the cell is negative.

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**Example 1.** Consider the following reaction.

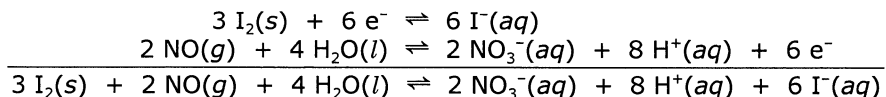


Derive this equation from half-cell equations and find  $E^\circ$  (in V) of the cell.  
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As usual, find the relevant half-reactions in Appendix C. You'll need to reverse one of them for oxidation, but it will be the higher one on the list in the Appendix.



As usual, to derive the balanced equation for the whole cell, set the loss equal to the gain. Take both of these to six electrons and then add the equations.



The sum of half-cell potentials will give you  $E^\circ = -0.42$  V for the cell. This is the same approach as for a galvanic cell.

You can also do nonstandard conditions.  
 .....

**Example 2.** Consider the same reaction as in Example 1. Find  $E$  for the following conditions.



As usual, this will involve Nernst,

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q$$

for which you already have  $E^\circ$  from Example 1. Plug everything in.

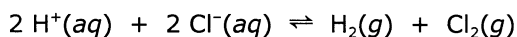
$$E = -0.42 \text{ V} - \frac{0.0257 \text{ V}}{6} \ln \frac{(0.00761)^2 (0.00861)^8 (0.0107)^6}{(0.0412)^2}$$

Solving this will get you  $E = -0.13 \text{ V}$ . If you wish to do this reaction at these conditions, you must send electrons into the cathode backed by a voltage of more than 0.13 V.

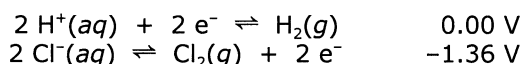
In reality, there are often issues which are involved in electrolytic applications which demand applied voltages in sizeable excess of a calculated amount, in order to achieve an appreciable rate of reaction. It was noted in Section 62.3 that the calculations of potential for galvanic cells give an open circuit potential, and that a real cell would produce less than that if a significant current was flowing. Likewise for electrolytics but now in the opposite direction, the voltage applied to the cell would have to be more than the calculated amount (even more than overmatching) in order to have a significant current and therefore a significant rate of reaction. The actual voltage may be a few tenths of a volt more than calculated, or it might be several volts more. There's always some resistance to moving ions around and this can take time to do; trying to push them around faster accounts for some inefficiencies and lost potential. Kinetic factors also come into play which are associated with the rate of electron transfer at an electrode surface. The kinetic issues overall can be substantial, and their effects increase at higher current flow; thus, a greater potential is needed as current increases for an electrolytic process. Collectively, the various factors give rise to what is called an overpotential: an overpotential is the difference between the necessary operational potential for a given cell and the thermodynamic potential as calculated by  $\Delta G = -nFE$ . Overpotentials can be very specific: they can depend on a specific half-reaction and they can also depend on the electrode material. Although overpotentials can be substantial for electrolytic applications and although this can result in sizeable energy losses during the operation, an overpotential can be advantageous in some circumstances. This is especially true for electrolyses in aqueous solutions, and it arises from the redox properties of water itself. The reduction of water produces  $\text{H}_2$  and the oxidation of water produces  $\text{O}_2$  but both of these are strongly subject to overpotentials. This will depend on the conditions (acidic or basic) and on the choice of electrode material. We can take advantage of water's overpotentials since that allows for other reductions or oxidations to occur instead.

Let's consider an example.

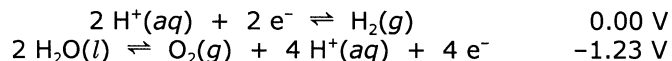
The electrolysis of hydrochloric acid produces hydrogen gas and chlorine gas.



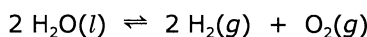
The half-reactions are



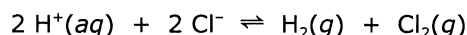
and  $E^\circ = -1.36 \text{ V}$  for the whole cell. But the electrolysis of water itself under acidic conditions should be easier in terms of the potential. The half-reactions are



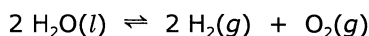
which leads to



for which  $E^\circ = -1.23 \text{ V}$  for the whole cell. Thus, based only on the thermodynamics of the potentials, if we apply a voltage of more than 1.36 V to the cell in an attempt to electrolyze  $\text{HCl}(\text{aq})$ ,



then we are also applying more than enough voltage to electrolyze water,



at least on a thermodynamic basis. But there is a large overpotential for  $\text{O}_2$  production, and the actual voltage which must be applied is typically greater than 1.23 V and it can easily be greater than 1.36 V. Thus, the overpotential prevents the production of  $\text{O}_2$ , or at least decreases it to a satisfactory level, and

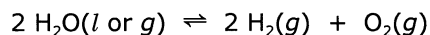
$\text{Cl}_2$  can be produced instead. Of course, the reaction you are trying to do may have its own overpotential, so you just have to pick the conditions which allow for the desired reaction, if that is possible (and it's not always possible). By the way, keep in mind that the potentials cited here are for standard conditions, and the conditions can often be varied to favor one reaction over another.

Overpotentials are not something easy to predict offhand, but it is important for you to at least be aware that they can occur. To make things manageable at this stage of the game, the common practice is to go with whatever reaction is given for a particular problem, without worrying about whether water is also reacting. Thus, if a problem dealt with the electrolysis of  $\text{HCl}(aq)$ , then you would set it up as above but without considering  $\text{O}_2$  production. On the other hand, if a problem specifically involves the electrolysis of water (as below), then go with that.

## 65.2 Applications

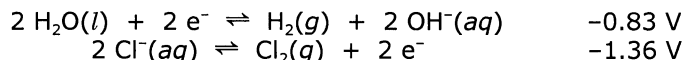
There are many, very important applications of electrolytic processes besides recharging a battery. There are quite a number of industrial uses; these produce a number of chemicals and goods, and many of these operations are on large scale. On such a scale, the electricity is a huge cost consideration, and those operations must take into account current, time and voltage or, simply, coulombs and volts or, more simply, the electrical joules (energy). Higher current flow requires even higher voltage due to higher overpotentials, so even that much becomes a trade-off for consideration in an actual setting.

The ultimate in electrolytic applications would be electrolysis of water itself to produce  $\text{H}_2$  and  $\text{O}_2$ , which is also known as water splitting.



As noted in Sections 50.3, 53.2 and 64.3,  $\text{H}_2$  is primarily produced from fossil fuels and that process releases massive amounts of  $\text{CO}_2$  into the environment. Production of  $\text{H}_2$  from electrolysis would decrease the  $\text{CO}_2$  burden but only to a limited extent: unfortunately, the electricity to power the electrolysis would still primarily derive from combustion of fossil fuels, and that would still release massive amounts of  $\text{CO}_2$ . One goal is to abundantly produce  $\text{H}_2$  from electrolysis of water using alternate sources of energy, which would eliminate generation and release of  $\text{CO}_2$  at any point in the process.  $\text{H}_2$  production is immensely important to human society, with most  $\text{H}_2$  going to the processing of fossil fuels and to the production of ammonia for fertilizer (Section 53.2). With fuel cells (Section 64.3),  $\text{H}_2$  could be an increasingly utilized source of clean, electrical energy. There is some production of  $\text{H}_2$  from electrolysis of water using renewable energy sources, but this pales in comparison to the amount produced from fossil fuels. Unfortunately, economics is a significant factor favoring fossil fuel sources, especially on the grandiose scale involved, but research is ongoing to change that. There are a number of variations in the design of the electrolytic cell system, including acid/base conditions, temperature and pressure. Significant overpotentials can also be involved, depending on the specific design, which represents added cost.

Aside from water splitting, one large industrial electrolytic process is the chloralkali process. "Chloralkali" is a contraction of chlorine and alkali; this process is the primary method of production of  $\text{Cl}_2$  and  $\text{NaOH}$ , both of which are used extensively as end products and also in the production of other compounds and goods, even something as common as liquid laundry bleach ("chlorine bleach") and some drain cleaners. The chloralkali process involves electrolysis of aqueous  $\text{NaCl}$ ;  $\text{Cl}^-$  is oxidized to  $\text{Cl}_2$  but  $\text{Na}^+$  does not react. Instead, water is reduced to  $\text{H}_2$  under basic conditions.



$\text{H}_2(g)$  and  $\text{Cl}_2(g)$  are produced, as well as more  $\text{OH}^-(aq)$ . The  $\text{OH}^-(aq)$  and the  $\text{Na}^+(aq)$  spectator ion constitute a solution of  $\text{NaOH}(aq)$ . Actual operating potentials are in the range of 3 - 4 V depending on the type of cell design. While this reaction is the primary method for producing  $\text{Cl}_2$  and  $\text{NaOH}$ , it also serves as a minor source for  $\text{H}_2$ . Again, this  $\text{H}_2$  is more costly than  $\text{H}_2$  from fossil fuels, but the  $\text{H}_2$  by this method (and from water splitting) contains fewer impurities than the  $\text{H}_2$  from fossil fuels; that difference is critical in some applications.

A number of metals are obtained industrially using electrolysis of an ionic compound; the metal cation is reduced to the metal elemental form while the anion is oxidized. Many of these processes require high potentials, much higher than even the overpotentials in water would allow. For this reason, these processes cannot use aqueous solutions. Instead, the electrolysis is done on the ionic compound itself. Ionic solids do not typically conduct electricity because the charges (ions) cannot move around in the solid phase. For this reason, the compounds are melted at high temperature, which allows the ions (and hence current) to flow. Aluminum is the largest-scale metal which is produced electrolytically, and

that scale is due to its immense applications as the metal itself or in alloys. Other metal elements which are produced electrolytically include Li, Na, Mg, etc. Numerous other metals are purified by electrolysis, such as Cu, Ag, Au, etc. These are done in aqueous electrolytic cells. The impure metal is the anode; the cathode is previously purified metal. The anode dissolves, the desired metal ion(*aq*) migrates to the cathode and is then reduced back to metal(*s*). Impurities remain dissolved or form an insoluble material.

Another application of electrolytic cells is metal plating. In metal plating, a thin coating of a metal is deposited onto a surface of some object, usually for protection or appearance. Many metals can be deposited as a plate, and you may be familiar with an object which is chrome-plated (chromium-plated) or silver-plated or gold-plated or whatever. The object on which the plate is formed is called the substrate. The substrate, which could be another metal or even a nonmetal material, is immersed into a plating bath which contains the ions of the metal to be plated. Those ions are then reduced and, with proper design, the elemental metal plates onto the substrate. The reduction can be done chemically by use of a suitable reducing agent, or the reduction can be done electrolytically by using the substrate itself as the cathode. The electrolytic route is called electroplating or electrodeposition. Electroplating is quite common, although it can only be used for metallic (conductive) substrates.

OK, we now change gears a bit. For several Chapters, we've discussed reactions, cell designs, and potentials, along with various applications of these things. Now we change the focus and start to consider the numbers of electrons which are involved and the current which delivers them.

### 65.3 Stoichiometry and other current aspects

The stoichiometric aspects of electrochemical processes involve more than just the usual stoichiometric things going back to Chapter 7. We now also consider the moles of electrons which are transferred and, along with time, the current. These aspects apply to galvanic and to electrolytic cells: for example, how long you can run a battery and how long you need to recharge it will deal with these issues. Here are a few extra points for echem stoichiometry.

As noted in Section 62.3, current is measured by amperage, with the amp as the standard unit.

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

or

$$C = A \times s$$

Again, coulomb is the unit of charge, here corresponding to electron charge and that connects to the number of electrons themselves. Notice the time term; time can also enter into a stoichiometry string. Time and current will give you an amount of electrons (in C) which have been transferred in a reaction.

Although the field of electricity has historically dealt with coulombs, chemists deal with moles. The typical stoichiometry problem will need a conversion step between the two. As we have seen, *F* is the connection

$$F = 96,485 \frac{C}{mol}$$

and it now serves as a unit conversion factor in a stoichiometry string in either of two forms.

$$\frac{96,485 C}{mol} \quad \text{OR} \quad \frac{mol}{96,485 C}$$

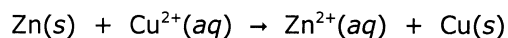
As for any stoichiometry problem, a balanced equation is needed. For echem, this can be for a whole reaction or just a single half-reaction. The value of *n* in the whole or half-reaction will be the moles of electrons transferred for the reaction as written. The reaction as written will involve some moles of reagents. Together, these will give the rxn ratio for the stoichiometry string.

Note that voltage is irrelevant for these calculations. We are now concerned with the number of electrons (as C or mol) which are transferred, and not how much push/pull is operating on them. In fact, the potential can change during the process, and that does not affect the stoichiometry aspects.

Now we consider several Examples illustrating the types of problems which can be encountered. We start with our first battery example.

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**Example 3.** The following cell uses Zn(*s*) and Cu(*s*) electrodes.



After the cell operates for 600. s at a current of 0.061 A, how many grams of the Zn electrode have reacted?

.....  
 You're given time and current and you need the amount of Zn which has reacted. As for any stoichiometry problem, this will involve a series of conversions. The amperage itself serves as a conversion factor, right-side up or upside down, as needed.

$$\frac{0.061 \text{ C}}{\text{s}} \quad \text{OR} \quad \frac{\text{s}}{0.061 \text{ C}}$$

We now start the stoichiometry string. The time and current will give you the amount of electrons in coulombs which have flowed.

$$\text{s} \rightarrow \text{C}$$

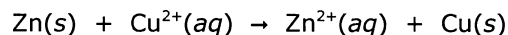
$$600. \text{ s} \times \frac{0.061 \text{ C}}{\text{s}}$$

We need the number of electrons in moles, so we bring in  $F$ .

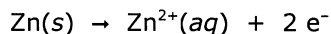
$$\text{s} \rightarrow \text{C} \rightarrow \text{mol } e^{-}$$

$$600. \text{ s} \times \frac{0.061 \text{ C}}{\text{s}} \times \frac{\text{mol } e^{-}}{96,485 \text{ C}}$$

This is the number of moles of electrons which were lost by Zn. Now, how many moles of Zn does that correspond to? For that, we bring in the rxn ratio. The rxn ratio connects mol  $e^{-}$  ( $n$ ) to mol Zn as given by a balanced equation. The balanced equation can be for a whole cell reaction or it can be for a half-reaction. In the present case, for



and using any of the ways illustrated in Example 5 in Chapter 63, you can find  $n = 2$  mol. Or you can focus on the half-reaction



which gives  $n = 2$  mol directly. Either way, the rxn ratio becomes the following.

$$\frac{2 \text{ mol } e^{-}}{\text{mol Zn}} \quad \text{OR} \quad \frac{\text{mol Zn}}{2 \text{ mol } e^{-}}$$

For the present stoichiometry string, you want the version on the right.

$$\text{s} \rightarrow \text{C} \rightarrow \text{mol } e^{-} \rightarrow \text{mol Zn}$$

$$600. \text{ s} \times \frac{0.061 \text{ C}}{\text{s}} \times \frac{\text{mol } e^{-}}{96,485 \text{ C}} \times \frac{\text{mol Zn}}{2 \text{ mol } e^{-}}$$

Final step: convert mol Zn to g Zn using molar mass.

$$\text{s} \rightarrow \text{C} \rightarrow \text{mol } e^{-} \rightarrow \text{mol Zn} \rightarrow \text{g Zn}$$

$$600. \text{ s} \times \frac{0.061 \text{ C}}{\text{s}} \times \frac{\text{mol } e^{-}}{96,485 \text{ C}} \times \frac{\text{mol Zn}}{2 \text{ mol } e^{-}} \times \frac{65.38 \text{ g Zn}}{\text{mol Zn}}$$

That's the whole string. Now plug and chug; you should get 0.012 g Zn. That is the amount of Zn(s) which has been oxidized to  $\text{Zn}^{2+}(aq)$  in the given time period with that amount of current.

A related type of calculation asks for time.

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**Example 4.** Consider the reaction for the lead-acid battery.



How much recharge time (in s) is needed to form 10.0 g Pb(s) using a current of 50.0 A?

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The recharge reaction is the reverse direction of the equation as written, but that does not change the stoichiometry aspect at all. You're given an amount of Pb to be made, and you need to find the time for it. This calculation goes in the backward direction relative to the calculation in Example 3.

Start with the given amount of Pb to be made; convert that to mol.

$$\begin{array}{l} \text{g Pb} \rightarrow \text{mol Pb} \\ 10.0 \text{ g Pb} \times \frac{\text{mol Pb}}{207.2 \text{ g Pb}} \end{array}$$

How many moles of electrons are needed for those moles Pb? You'll need a rxn ratio which incorporates the value of  $n$ ; for the equation as written,  $n = 2$  mol.

$$\begin{array}{l} \text{g Pb} \rightarrow \text{mol Pb} \rightarrow \text{mol e}^- \\ 10.0 \text{ g Pb} \times \frac{\text{mol Pb}}{207.2 \text{ g Pb}} \times \frac{2 \text{ mol e}^-}{\text{mol Pb}} \end{array}$$

This gives the number of moles of electrons which are needed. Convert that to coulombs via  $F$ .

$$\begin{array}{l} \text{g Pb} \rightarrow \text{mol Pb} \rightarrow \text{mol e}^- \rightarrow \text{C} \\ 10.0 \text{ g Pb} \times \frac{\text{mol Pb}}{207.2 \text{ g Pb}} \times \frac{2 \text{ mol e}^-}{\text{mol Pb}} \times \frac{96,485 \text{ C}}{\text{mol e}^-} \end{array}$$

Those coulombs will connect to time by the given current. The current will go in upside down for this string.

$$\begin{array}{l} \text{g Pb} \rightarrow \text{mol Pb} \rightarrow \text{mol e}^- \rightarrow \text{C} \rightarrow \text{s} \\ 10.0 \text{ g Pb} \times \frac{\text{mol Pb}}{207.2 \text{ g Pb}} \times \frac{2 \text{ mol e}^-}{\text{mol Pb}} \times \frac{96,485 \text{ C}}{\text{mol e}^-} \times \frac{\text{s}}{50.0 \text{ C}} \end{array}$$

There's your string and that gets you 186 s as your answer.

Your turn.

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**Example 5.** You wish to electroplate 0.048 g Ag(s) onto a substrate, starting from  $\text{Ag}^+(\text{aq})$ . How much time (in s) is needed for the process using a current of 0.063 A?

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You are only given enough information to set up a half-reaction, and that's all you need here. Write out the balanced half-reaction.

Set up your string and go.

If you run into trouble, the setup here is just like Example 4; look at that if you need to. You should get 680 s for your answer.

These Examples represent the types of problems which can be encountered. These stoichiometry aspects have actually entered into consumer goods, even though you may not be aware of it. Many rechargeable batteries carry a specification for capacity; the capacity is the amount of charge it can deliver over its useful operating range, starting from a recharged condition. That capacity relates to the masses of the reagents which are present inside the battery. Capacities are commonly expressed as current • time. For example, common NMH batteries often show a capacity rating expressed as mAh on their label or package. mAh? The mA part is milli-amp while h is hour, so mAh is milliamp • hour and that is current • time. Given that information, you can calculate the number of moles of electrons which are available during typical use.

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**Example 6.** A capacity rating for a particular brand's AA NMH battery is 2,500 mAh. How many mol  $e^-$  is that?  
 .....

This is again a problem which involves current and time. Before we set up, let's take care of the milli part: 2,500 mAh = 2.5 Ah. Now go.

The unit of A is C/s, so the overall units right now are (C/s) • h.

$$\frac{2.5 \text{ C} \cdot \text{h}}{\text{s}}$$

Convert h to s in order to cancel the time units.

$$\frac{2.5 \text{ C} \cdot \text{h}}{\text{s}} \times \frac{3600 \text{ s}}{\text{h}}$$

Convert C to mol.

$$\frac{2.5 \text{ C} \cdot \text{h}}{\text{s}} \times \frac{3600 \text{ s}}{\text{h}} \times \frac{\text{mol } e^-}{96,485 \text{ C}}$$

Right now, this stands at mol  $e^-$  and that is the requested info. Punch that out to get 0.093 mol  $e^-$ . The battery can deliver 0.093 mol  $e^-$  within a specified voltage range, starting from a fresh charge. Capacity is a useful consideration for a consumer, and it is one criterion to be aware of when selecting batteries and brands.

OK, time for our final topic. This one deals with an unfortunate reality.

## 65.4 Corrosion

Corrosion refers to a chemical reaction which occurs between a solid material and components in its environment, and which can degrade or ultimately consume that solid. In the case of metals, these are redox reactions and they can involve current flow between different parts of the system. Atmospheric  $\text{O}_2(g)$  is the primary culprit, acting as the ultimate oxidant in most cases. Other oxidants can sometimes get involved, such as  $\text{H}^+(aq)$ , especially in an acidic environment.

Rusting is the most obvious example. Rusting of iron-based structures is a very costly loss to human society every year, and even the efforts to inhibit rust run into many billions of dollars annually. Attempts to inhibit rust take many forms, with varying levels of success and at varying expense. Rusting is not a single reaction; instead, it is a process involving several reactions which ultimately oxidize Fe and reduce  $\text{O}_2$ . Furthermore, "rust" is not a single, chemical compound and it does not have a specific composition. It is a mixed precipitate of  $\text{Fe}^{3+}$ , perhaps with some  $\text{Fe}^{2+}$ , with anions of  $\text{O}^{2-}$  and/or  $\text{OH}^-$ , and often  $\text{H}_2\text{O}$  acting as a ligand or in some other role within the solid. The composition can vary depending on the circumstances of formation, such as pH and the availability of  $\text{O}_2$ . A general formula of  $\text{Fe}_2\text{O}_3(\text{H}_2\text{O})_x$  is often cited as representative of the substances involved. The rusting of iron requires  $\text{O}_2$  and it requires  $\text{H}_2\text{O}$ . Even a thin film of moisture from humidity in the air allows for some rusting. On the other hand, in dry air, iron does not rust at all.

Before looking more at rusting, let's consider metals which do not corrode in a similar manner.

Some metals, such as gold and platinum, are not readily oxidized under naturally encountered conditions, for thermodynamic reasons. Thus, they can be found as elemental Au(s) and Pt(s). Most metals, however, can be oxidized under naturally encountered conditions, and many have a strong driving force to do so, such as zinc or aluminum. But even these do not typically corrode into a flaky, crusty heap as occurs for rust. The reason for this is that, as their surface oxidizes, an insoluble oxide product is formed which adheres tightly to the surface of the underlying metal and protects the metal from further exposure to  $\text{O}_2$  and/or  $\text{H}_2\text{O}$ . This process is called passivation; the surface is rendered passive to further oxidation. The protective layer is very thin, commonly in the nm range, and it is too thin to be seen by eye. Even aluminum foil has such a passivation layer on it but you can't see the layer itself. If you scratch through the protective layer on a metal, the scratch exposes fresh metal but this again passivates. In an environment which is sufficiently acidic or basic, however, the protective layer itself can react and dissolve, ultimately leading to continued reaction of the metal solid. The extent of this will depend on the metal and the various solubility equilibria which would apply at a given pH. As one example, the passivation of aluminum can be defeated in either pH direction: at low pH, the passivation layer is

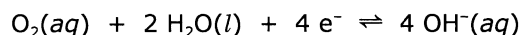
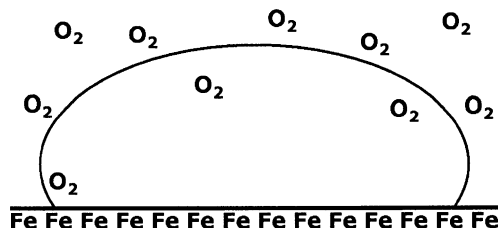


neutralized and it dissolves to give  $\text{Al}^{3+}(\text{aq})$ ; at high pH, soluble complexes are formed such as  $\text{Al}(\text{OH})_4^-(\text{aq})$ . In either case, without its passivation layer, the  $\text{Al}(\text{s})$  continues to oxidize and dissolve, exposing more Al metal.

Fortunately, most metals which can react with air will instead passivate under typical conditions. Ironically and unfortunately, iron does a poor job of this, and iron is the world's leading structural metal. Let's take a look at iron and the rusting process.

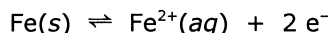
We start with a drop of water on a piece of iron, all of which is exposed to air, as shown at right. Some  $\text{O}_2(\text{g})$  from the air dissolves into the water. This solution can function as an electrochemical cell, and various half-reactions are available.

The ultimate oxidant is  $\text{O}_2$ , whose reduction gives  $\text{OH}^-(\text{aq})$ .



This reaction increases the pH.

The oxidation of  $\text{Fe}(\text{s})$  gives  $\text{Fe}^{2+}(\text{aq})$ .

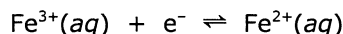


Iron atoms from the surface of the metal oxidize and dissolve to form  $\text{Fe}^{2+}(\text{aq})$  ions. The entire chunk of  $\text{Fe}(\text{s})$  is a conductor, so the electrons can come from anywhere on the surface and any iron atom along the surface can dissolve.

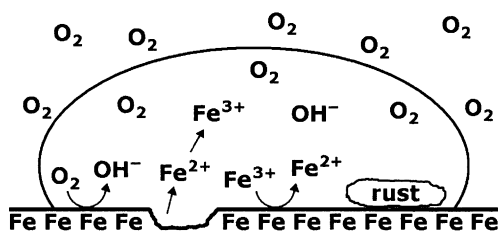
OK, so far, this description is similar for iron and for many metals which do passivate. For most metals, however, the metal cations and the basic conditions provide an insoluble protective layer of metal oxide or hydroxide film. But the iron(II) oxides/hydroxides are vulnerable to further oxidation and do not provide a lasting passivation layer, thus allowing more iron metal to react. Furthermore,  $\text{Fe}^{3+}(\text{aq})$  can get involved from oxidation of  $\text{Fe}^{2+}$  (using more  $\text{O}_2$ )



and the  $\text{Fe}^{3+}$  ions can also oxidize the Fe metal surface to form more  $\text{Fe}^{2+}(\text{aq})$ .



These two half-reactions are the reverse of each other, but they derive from different reactions, one involving  $\text{O}_2(\text{aq})$  and the other involving  $\text{Fe}(\text{s})$ . For the latter, the electron can again come from anywhere on the  $\text{Fe}(\text{s})$  surface.



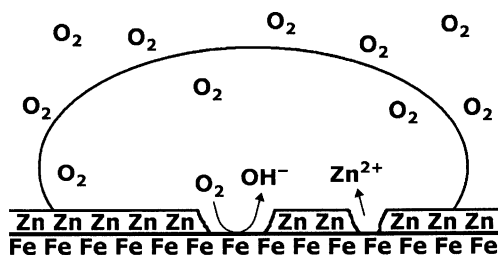
Somewhere along the way, a precipitate starts to form, mostly of iron(III) oxides/hydroxides. This precipitate does not adhere well either, so the total corrosion process simply continues. This gives rust. A schematic of the various processes is shown at left.

Needless to say, protecting iron is of tremendous interest. There are numerous methods to inhibit rust, many of which are physical but some are also electrochemical. The physical approaches simply block moisture and/or  $\text{O}_2$  from contacting the metal surface. One of the oldest and easiest short-term methods for protection of iron-based tools has been to coat them with oil;  $\text{O}_2$  will still dissolve into oil and reach the metal surface, but water will not. Another common practice for many metal objects is paint, and you are well familiar with painted metal surfaces, big and small, including bridge beams, some vehicles, etc. These coatings are good as long as they stay intact, but scratches will expose fresh metal and can start the rusting process.

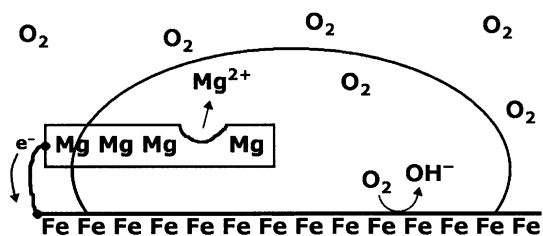
Besides the physical methods, electrochemical protection is also available in different forms. These methods do not depend on total surface coverage.

Galvanization has long been used to protect iron items. This involves coating an iron object with  $\text{Zn}(\text{s})$ , either by electrolysis (electrogalvanizing) or by dipping the object into molten Zn (hot dip galvanizing). (You can even find these terms on a simple box of nails which are intended for outdoor

applications.) The surface of the zinc coating which is exposed to air is passivated. If the zinc coats the object fully, then that physical coverage is again preventing direct reaction between air, moisture and iron. On the other hand, if there is a scratch through the zinc, then iron is exposed and oxidation can occur. When that happens, electrochemical protection kicks in. The zinc is still passivated on its exposed surface, but its other surface is joined to iron and the joined metals are fully conductive. Although  $O_2$  can take electrons from the exposed Fe surface, the electrons ultimately come from the zinc because zinc is a better reducing agent than iron. Thus,  $Zn^{2+}$  dissolves. A general schematic is shown at right. (The metal layers are enormously thicker than just one atom. The passivation layer on Zn is not shown.) Over time, the zinc coating does erode, but it greatly extends the lifetime of the iron object which it was protecting.



Another electrochemical approach uses sacrificial anodes. These are simply pieces of metals which are more reactive and more strongly reducing compared to Fe, such as Mg, Zn or Al, or alloys thereof. These metals are electrically connected to the iron item by wiring or by direct attachment; they are also in the same aqueous environment as the iron item in order to allow for ion flow. A general schematic is shown at left. Sacrificial anodes are not intended to



give much direct coverage, but they do provide electrons to iron when it is under attack by  $O_2$ . They are called anodes because they are oxidized; they are called sacrificial because they are sacrificed to protect the iron item. This method has very long term utility, because the anodes can be replaced periodically. The uses of sacrificial anodes range from water heaters in homes to hulls of large oceanic ships and also to oil rigs in open water. Such anodes are even used for

protecting shipwrecks: once a sunken ship is found and which is of study or preservation interest, they can connect large chunks of sacrificial anodes to the ship while it is still underwater, until it can be recovered. (This won't work for wooden ships or other nonconducting materials.) By the way, marine applications for corrosion protection are much more demanding than those in fresh water. Salt accelerates rusting tremendously, a problem also encountered in cities and other areas which salt their roads in the wintertime.

Sacrificial anodes are a form of cathodic protection, although those terms may sound like a contradiction. The iron is the site of reduction of  $O_2$  and that means the iron is the cathode; since the iron is being protected, the more general term is cathodic protection. In addition to the use of sacrificial anodes, cathodic protection can also be done using a DC power source. The iron item to be protected is connected to the negative side of DC; the positive side of DC is attached to another metal object which is sacrificed. (This could even be cheap scrap iron.) The power source keeps a supply of electrons going to the iron to be protected. To maintain conductivity, both metal objects must again be in the same aqueous environment. Underground metal pipework can be protected in this manner, in which case groundwater serves as the aqueous environment.

These are some of the numerous methods which are used to protect iron structures from rust. The irony remains that iron is the leading structural metal despite its unusual property of corroding readily in typical environments. Although other metals could be used structurally with much less corrosion problem, those are much more expensive. Thus, there is a trade-off and a balance. Even stainless steel is considerably more expensive; this is still mostly iron but chromium, and often other elements, has been added. Cr at the surface oxidizes to form a much better passivation layer than iron, and the metal has far better durability.

#### 65.4 Another closing

We now complete five Chapters of many things electrochemical. As you can see, there are a large number of reactions which can be involved and there are a large number of applications which are vastly important to human society. Although  $E$  and  $V$  are a major focal point in these studies,  $E$  yet derives from  $\Delta G$ , and  $\Delta G$  still rules. But, again, even  $\Delta G$  derives from  $\Delta S_{univ}$ .

These things are part of your world. A really big part.

Next: a return journey to the center.

### Problems

- True or false.
  - An electrolytic reaction is exergonic.
  - In an electrolytic cell, electrons flow from the cell cathode to the cell anode.
  - Metal plating can be done electrolytically.
  - During rusting,  $\text{Fe}^{2+}$  is reduced.
  - Magnesium can act as a sacrificial anode for iron.
- The following equations represent cell reactions. All reagents are listed but the equations may not be balanced. For each cell reaction, indicate whether the reaction would be exergonic or endergonic at standard conditions.
  - $\text{Sn}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Sn}(\text{s}) + \text{Fe}^{2+}(\text{aq})$
  - $\text{I}_2(\text{s}) + \text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{I}^{-}(\text{aq})$
  - $\text{Cr}^{3+}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Cr}^{2+}(\text{aq}) + \text{Fe}^{3+}(\text{aq})$
  - $\text{SO}_4^{2-}(\text{aq}) + \text{MnO}_2(\text{s}) + \text{OH}^{-}(\text{aq}) \rightarrow \text{MnO}_4^{-}(\text{aq}) + \text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
  - $\text{Br}^{-}(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{Br}_2(\text{l}) + \text{Cl}^{-}(\text{aq})$
- Consider the following balanced equation.
 
$$\text{ClO}_3^{-}(\text{aq}) + 3 \text{H}_2\text{O}(\text{l}) + 6 \text{Br}^{-}(\text{aq}) \rightarrow \text{Cl}^{-}(\text{aq}) + 6 \text{OH}^{-}(\text{aq}) + 3 \text{Br}_2(\text{l})$$
 The cell is operated at the following conditions.  
 $[\text{ClO}_3^{-}] = 0.0113 \text{ M} \quad [\text{Br}^{-}] = 0.00822 \text{ M} \quad [\text{Cl}^{-}] = 0.00449 \text{ M} \quad \text{pH} = 10.30$ 
  - What is  $E^{\circ}$  (in V)?
  - What is  $E$  (in V) for the given conditions?
  - What is the value of  $K$ ?
- Consider the following balanced equation.
 
$$2 \text{Fe}^{3+}(\text{aq}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{Fe}(\text{s}) + 6 \text{H}^{+}(\text{aq})$$
 The cell is operated at the following conditions.  
 $[\text{Fe}^{3+}] = 0.0146 \text{ M} \quad P(\text{H}_2) = 0.661 \text{ atm} \quad [\text{H}^{+}] = 0.00439 \text{ M}$ 
  - What is  $E^{\circ}$  (in V)? Is the reaction exergonic or endergonic at standard conditions?
  - What is  $E$  (in V) for the given conditions? Is the reaction exergonic or endergonic at the given conditions?
- Silver oxide button batteries come in a variety of sizes and capacities. One brand lists a watch battery with a capacity of 28 mAh.
  - How many mol  $\text{e}^{-}$  does that correspond to?
  - How much  $\text{Ag}(\text{s})$  (in g) would be produced for that capacity?
- Chrome plating can be done electrolytically by reduction of either  $\text{CrO}_4^{2-}$  or of  $\text{Cr}^{3+}$ . This is used for protection of iron substrates, and it is also done for appearance since a very shiny finish is obtained. Consider an electrolytic cell for plating Cr metal from  $\text{CrO}_4^{2-}(\text{aq})$ . How much  $\text{Cr}(\text{s})$  (in g) can be plated using a current of 2.33 A for 10.0 minutes?
- Nickel can also be used for electroplating iron-based objects. How much time (in min) is required to plate 1.00 g  $\text{Ni}(\text{s})$  from a solution of  $\text{Ni}^{2+}(\text{aq})$ , using a current of 4.50 A?