

Electrochemistry

a Chem1 Supplement Text

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1 Chemistry and electricity

The connection between chemistry and electricity is a very old one, going back to Allesandro Volta's discovery, in 1793, that electricity could be produced by placing two dissimilar metals on opposite sides of a moistened paper. In 1800, Nicholson and Carlisle, using Volta's primitive battery as a source, showed that an electric current could decompose water into oxygen and hydrogen. This was surely one of the most significant experiments in the history of chemistry, for it implied that the atoms of hydrogen and oxygen were associated with positive and negative electric charges, which must be the source of the bonding forces between them. By 1812, the Swedish chemist Berzelius could propose that all atoms are electrified, hydrogen and the metals being positive, the nonmetals negative. In electrolysis, the applied voltage was thought to overpower the attraction between these opposite charges, pulling the electrified atoms apart in the form of *ions* (named by Berzelius from the Greek for "travellers"). It would be almost exactly a hundred years later before the shared electron pair theory of G.N. Lewis could offer a significant improvement over this view of chemical bonding.

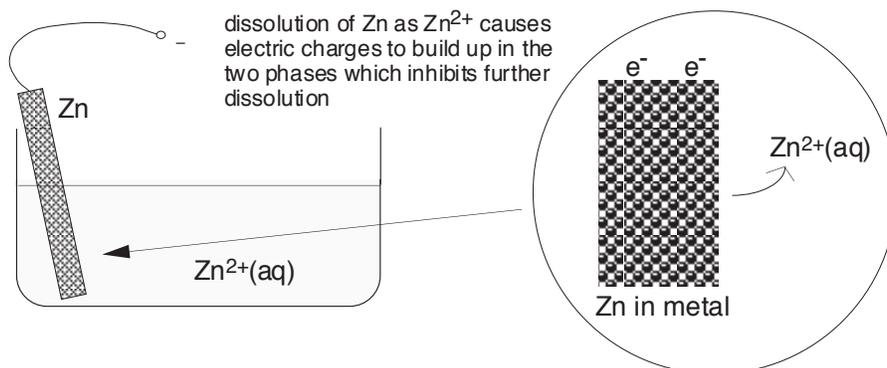


Figure 1: Oxidation of metallic zinc in contact with water

Meanwhile, the use of electricity as a means of bringing about chemical change continued to play a central role in the development of chemistry. Humphrey Davy prepared the first elemental sodium by electrolysis of a sodium hydroxide melt. It was left to Davy's former assistant, Michael Faraday, to show that there is a quantitative relation between the amount of electric charge and the quantity of electrolysis product. James Clerk Maxwell immediately saw this as evidence for the "molecule of electricity", but the world would not be receptive to the concept of the electron until the end of the century.

Electroneutrality

Nature seems to very strongly discourage any process that would lead to an excess of positive or negative charge in matter. Suppose, for example, that we immerse a piece of zinc metal in pure water. A small number of zinc atoms go into solution as Zn^{2+} ions, leaving their electrons behind in the metal:



As this process goes on, the electrons which remain in the zinc cause a negative charge to build up which makes it increasingly difficult for additional positive ions to leave the metallic phase. A similar buildup of positive charge in the liquid phase adds to this inhibition. Very soon, therefore, the process comes to a halt, resulting in a solution in which the concentration of Zn^{2+} is so low (around $10^{-10} M$) that the water can still be said to be almost "pure".

There would be no build-up of charge if the electrons could be removed from the metal as the positive ions go into solution. One way to arrange this is to drain off the excess electrons through an external circuit that forms part of a complete electrochemical cell; this we will describe later. Another way to remove electrons is to bring a good electron acceptor (that is, an *oxidizing agent*) into contact with the electrode. A

suitable electron acceptor would be hydrogen ions; this is why acids attack many metals. For the very active metals such as sodium, H_2O is a sufficiently good electron acceptor.

The degree of charge unbalance that is allowed produces differences in electric potential of no more than a few volts, and corresponds to concentration unbalances of oppositely charged particles that are not even detectable by ordinary chemical means. There is nothing mysterious about this prohibition, known as the *electroneutrality principle*; it is a simple consequence of the thermodynamic work required to separate opposite charges, or to bring like charges into closer contact. The additional work raises the free energy ΔG of the process, making it less spontaneous.

The only way we can get the reaction in Eq 1 to continue is to couple it with some other process that restores electroneutrality to the two phases. A simple way to accomplish this would be immerse the zinc in a solution of copper sulfate instead of pure water. As you will recall if you have seen this commonly-performed experiment carried out, the zinc metal quickly becomes covered with a black coating of finely-divided metallic copper. The reaction is a simple oxidation-reduction process, a transfer of two electrons from the zinc to the copper:



The dissolution of the zinc is no longer inhibited by a buildup of negative charge in the metal, because the excess electrons are removed from the zinc by copper ions that come into contact with it. At the same time, the solution remains electrically neutral, since for each Zn^{2+} introduced to the solution, one Cu^{2+} is removed. The net reaction



quickly goes to completion.

Potential differences at interfaces

Electrochemistry is the study of reactions in which charged particles (ions or electrons) cross the interface between two phases of matter, typically a metallic phase (the *electrode*) and a conductive solution, or *electrolyte*. A process of this kind is known generally as an *electrode process*.

Electrode processes (reactions) take place at the surface of the electrode, and produce a slight unbalance in the electric charges of the electrode and the solution. The result is an *interfacial potential difference* which, as we saw above, can materially affect the rate and direction of the reaction. Much of the importance of electrochemistry lies in the ways that these potential differences can be related to the thermodynamics and kinetics of electrode reactions. In particular,

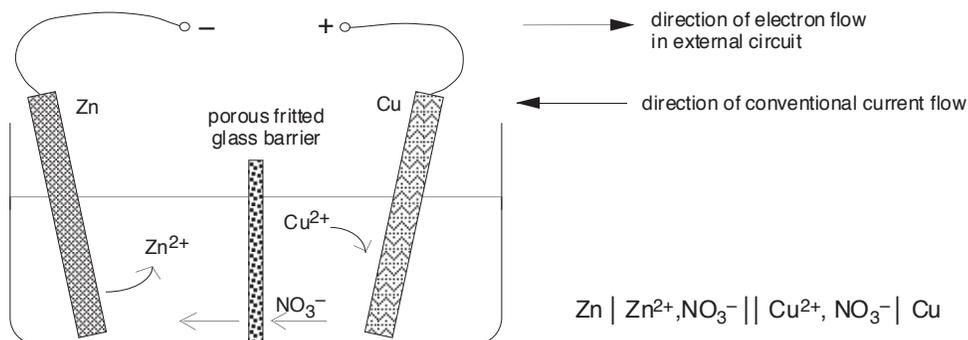


Figure 2: A simple electrochemical cell

manipulation of the interfacial potential difference affords an important way of exerting external control on an electrode reaction.

The interfacial potential differences which develop in electrode-solution systems are limited to only a few volts at most. This may not seem like very much, but it is important to understand that what is important is the *distance* over which this potential difference exists. In the case of an electrode immersed in a solution, this distance corresponds to the thin layer of water molecules and ions that attach themselves to the electrode surface—normally only a few atomic diameters. In this way a very small voltage can produce a very large *potential gradient*. For example, a potential difference of one volt across a thickness of only 10^{-8} cm amounts to a *potential gradient* of 100 million volts per centimetre: a very significant value indeed!

Actually, interfacial potentials exist between *any* two phases in contact, even in the absence of chemical reactions. In many forms of matter, they are the result of adsorption or ordered alignment of molecules caused by non-uniform forces in the interfacial region. Thus colloidal particles in aqueous suspensions selectively adsorb a given kind of ion, positive for some colloids, and negative for others. The resulting net electric charge prevents the particles from coming together and coalescing, which they would otherwise tend to do under the influence of ordinary van der Waals attractions.

2 Electrochemical cells

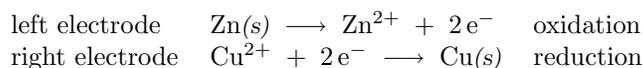
The electron-transfer reactions that occur at the surface of a metal immersed in a solution take place near the surface of the electrode, so there is no way that the electrons passing between the solution and the electrode can be channeled through an instrument to measure their voltage or to control the rate of the reaction. However, if we have *two* such metal-solution interfaces, we can easily measure a potential difference between them. Such an arrangement is called a

galvanic cell. A typical cell might consist of two pieces of metal, one zinc and the other copper, each immersed each in a solution containing a dissolved salt of the corresponding metal (see Fig. 2). The two solutions are connected by a tube containing a porous barrier that prevents them from rapidly mixing but allows ions to diffuse through.

If we simply left it at that, each metal would just sit in its own solution, and no significant amount of reaction would take place. However, if we connect the zinc and copper by means of a metallic conductor, the excess electrons that remain when Zn^{2+} ions go into solution in the left cell would be able to flow through the external circuit and into the right electrode, where they could be delivered to the Cu^{2+} ions that are converted into Cu atoms at the surface of the copper electrode. The net reaction is the same as before:



but this time, the oxidation and reduction steps take place in separate locations:



An electrochemical cell affords us a high degree of control and measurement of the cell reaction. If the external circuit is broken, the reaction stops. If we place a variable resistance in the circuit, we can control the rate of the cell reaction by simply turning a knob. By connecting a battery or other source of current to the two electrodes, we can even force the reaction to proceed in its non-spontaneous, or reverse direction.

By placing an ammeter in the external circuit, we can measure the amount of electric charge that passes through the electrodes, and thus the number of moles of reactants that get transformed into products in the cell reaction.

Electric charge q is measured in *coulombs*. The amount of charge carried by one mole of electrons is known as the *faraday*, which we denote by \mathcal{F} . Careful experiments have determined that

$$\boxed{1 \mathcal{F} = 96467 \text{ c}}$$

For most purposes, you can simply use 96,500 c as the value of the faraday.

When we measure electric current, we are measuring the rate at which electric charge is transported through the circuit. A current of one ampere corresponds to the flow of one coulomb per second.

Problem Example 1 _____

In the cell of Fig. 2, how much mass would the zinc electrode lose if a current of 0.15 amp flows through the external circuit for 1.5 hours?

Solution. The amount of charge passing between the electrodes is

$$(0.15 \text{ amp}) \times (5400 \text{ sec}) = 810 \text{ c}$$

or

$$(810 \text{ c}) / (96500 \text{ c } \mathcal{F}^{-1}) = .0084 \mathcal{F}$$

Since the oxidation of one mole of Zn to Zn^{2+} results in the removal of two moles of electrons, the number of moles of Zn removed from the electrode is 0.0042, corresponding to a weight loss of

$$(.0042 \text{ } M) \times (65.37 \text{ g } M^{-1}) = .275 \text{ g}$$

Transport of charge within the cell

In order for the cell of Fig. 2 to operate, not only must there be an external electrical circuit between the two electrodes, but the two electrolytes (the solutions) must be in contact. The need for this can be understood by considering what happens to the two solutions as the cell reaction proceeds. Positive charge (in the form of Zn^{2+}) is added to the electrolyte in the left compartment, and removed (as Cu^{2+}) from the right side. Left unchecked, this would produce the same effect as disconnecting the electrodes: the amount of work required to introduce additional Zn^{2+} ions into the positively-charged electrolyte would increase, and addition of electrons to Cu^{2+} ions on the right would be similarly inhibited.

Put in a slightly different way, the charge carried by the electrons through the external circuit must be accompanied by a compensating transport of ions between the two cells. This means that we must provide a path for ions to move directly from one cell to the other. This ionic transport involves not only the electroactive species Cu^{2+} and Zn^{2+} , but also the counterions, which in this example are NO_3^- . Thus an excess of Cu^{2+} in the left compartment could be alleviated by the drift of these ions into the right side, or equally well by diffusion of nitrate ions to the left. More detailed studies reveal that both processes occur, and that the relative amounts of charge carried through the solution by positive and negative ions depends on their relative *mobilities*, which express the velocity with which the ions are able to make their way through the solution. Since negative ions tend to be larger than positive ions, the latter tend to have higher mobilities and carry the larger fraction of charge.

In the simplest cells, the barrier between the two solutions can be a porous membrane, but for precise measurements, a more complicated arrangement, known as a *salt bridge*, is used. The salt bridge consists of an inverted U-tube (Fig. 4) filled with a concentrated solution of KCl and fitted with porous barriers at each end. The purpose of the salt bridge is to minimize the natural potential difference, known as the

junction potential, that develops (as mentioned in the previous section) when any two phases (such as the two solutions) are in contact. This potential difference would combine with the two half-cell potentials so as to introduce a degree of uncertainty into any measurement of the cell potential. With the salt bridge, we have two liquid junction potentials instead of one, but they tend to cancel each other out.

Cell description conventions

In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopted. In this notation the cell of Fig. 2 would be



In this notation, the vertical bars indicate *phase boundaries*; the double vertical bar in the middle denotes the phase boundary between the two solutions. As a matter of convention, the chemical species that undergo *reduction* when the cell reaction proceeds to the right according to the net equation are shown on the *right* side, and those that undergo *oxidation* are shown on the *left*. Note carefully that this is entirely independent of the physical location of the two electrodes in the actual cell in Fig. 2.

There are several other conventions relating to cell notation and nomenclature that you are expected to know:

- The *anode* is where *oxidation* occurs, and the *cathode* is the site of *reduction*. In an actual cell, either electrode can have either identity, depending on the direction in which the net cell reaction is occurring.
- If electrons flow from the left electrode to the right electrode when the cell operates in its spontaneous direction, the potential of the right electrode will be higher than that of the left, and the cell potential will be *positive*.
- “Conventional current flow” is from positive to negative, which is opposite to the direction of the electron flow. This means that if the electrons are flowing from the left electrode to the right, a galvanometer placed in the external circuit would indicate a current flow from right to left.

Electrodes and electrode reactions

The electron-transfer step that takes place at each electrode is known as the *electrode reaction*. The substance that loses or receives the electron is called the *electroactive species*.

In the example of the Zn/Cu cell we have been using, the electrode reaction involves a metal and its hydrated cation; we call such electrodes *metal-metal ion* electrodes. There are a number of other kinds of electrodes which are widely encountered in electrochemistry and analytical chemistry.

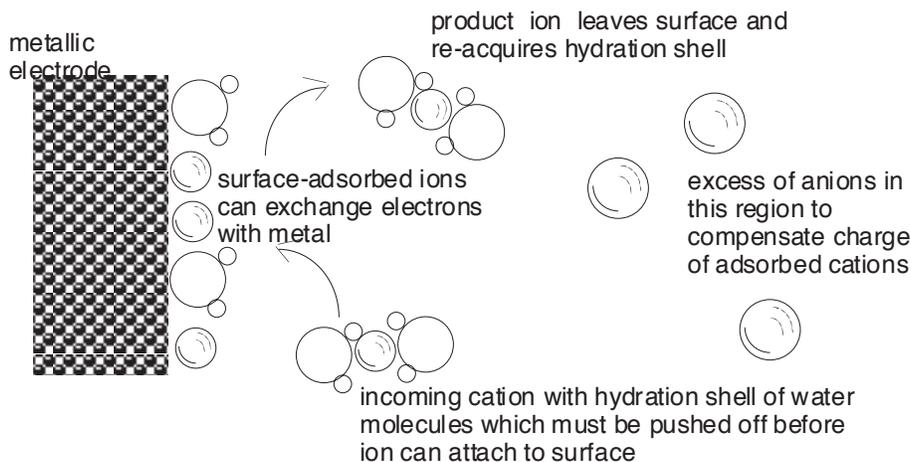
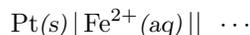


Figure 3: Electron-transfer at an electrode

Ion-ion electrodes Many electrode reactions involve only ionic species, such as Fe^{2+} and Fe^{3+} . If neither of the electroactive species is a metal, some other metal must serve as a conduit for the supply or removal of electrons from the system. In order to avoid complications that would arise from electrode reactions involving this metal, a relatively inert substance such as platinum is commonly used. Such a half cell would be represented as

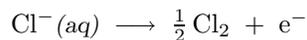


and the half-cell reaction would be



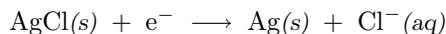
The reaction occurs at the surface of the electrode (Fig. 3). The electroactive ion diffuses to the electrode surface and adsorbs (attaches) to it by van der Waals and coulombic forces. In doing so, the waters of hydration that are normally attached to any ionic species must be displaced. This process always costs energy; if a lot of work is required, then only a small fraction of the ions will attach to the surface long enough to undergo electron transfer, and the reaction will be slow. The actual electron-transfer occurs by quantum-mechanical tunnelling.

Gas electrodes Some electrode reactions involve a gaseous species such as H_2 , O_2 , or Cl_2 . Such reactions must also be carried out on the surface of a metallic conductor such as platinum. A typical reaction of considerable commercial importance is

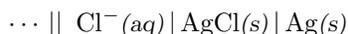


Similar reactions involving the oxidation of $\text{Br}_2(l)$ or $\text{I}_2(s)$ also take place at platinum surfaces.

Insoluble-salt electrodes A typical electrode of this kind consists of a silver wire covered with a thin coating of silver chloride, which is insoluble in water. The electrode reaction consists in the oxidation and reduction of the silver:



The half cell would be represented as



Although the usefulness of such an electrode may not be immediately apparent, this kind of electrode finds very wide application in electrochemical measurements, as we shall see later.

3 Standard half-cell potentials

Although many applications of electrochemical cells involve a flow of current between the two electrodes, the most fundamental kind of measurement we can make is of the voltage, or EMF between the electrodes in the absence of any cell current. This voltage, which we usually refer to as the *cell potential*, is the potential difference between the electrodes, and is the difference between the *half-cell potentials* of the right and left sides:

$$E_{\text{cell}} = \Delta V = V_{\text{right}} - V_{\text{left}} \quad (2)$$

Each of the half-cell potentials is in turn a potential difference between the electrode and the solution, so for our example cell the above relation can be expanded to

$$E_{\text{cell}} = V_{\text{Cu}} - V_{\text{soln}} + V_{\text{soln}} - V_{\text{Zn}} \quad (3)$$

It is important to understand that individual half-cell potentials are not directly measurable; there is no way you can determine the potential difference between a piece of metal and a solution. Attaching one lead of a voltmeter to the metal and dipping the other in the solution would simply create a new half-cell involving the immersed metallic conductor.

The fact that individual half-cell potentials are not directly measurable does not prevent us from defining and working with them. If we cannot determine the absolute value of a half-cell potential, we can still measure its value in relation to the potentials of other half cells. In particular, if we adopt a reference half-cell whose potential is arbitrarily defined as zero, and measure the potentials of various other electrode systems against this reference cell, we are in effect

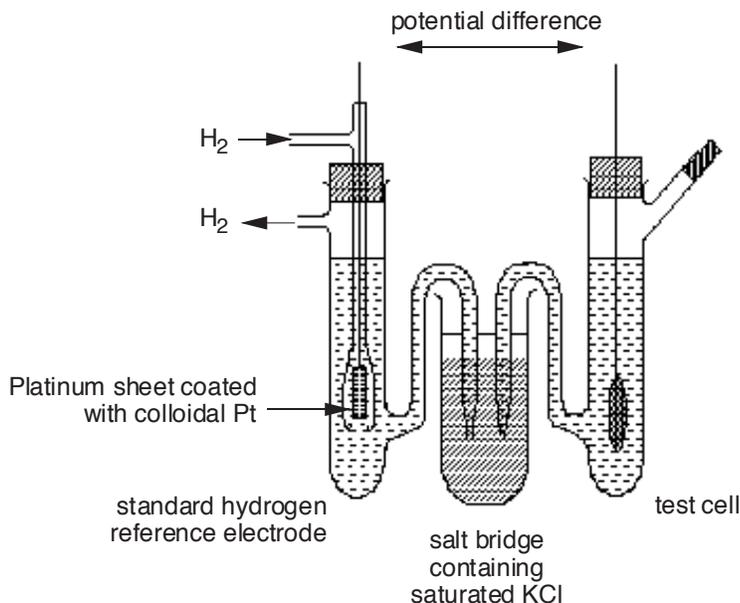


Figure 4: Cell for measurement of standard potentials

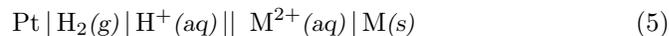
measuring the half-cell potentials on a scale that is relative to the potential of the reference cell.

As a reference cell we use the half cell whose reaction is



This is the *hydrogen electrode*, an example of a gas electrode as was discussed above. When this electrode is set up under standardized conditions, it becomes the *standard hydrogen electrode*, sometimes abbreviated *SHE*.

In order to measure the relative potential of some other electrode M^{2+}/M , we can set up a cell



whose net reaction is



In analogy with Eq 3, the potential difference between the platinum and M electrodes will be

$$E_{\text{cell}} = V_{\text{M}} - V_{\text{soln}} + V_{\text{soln}} - V_{\text{Pt}}$$

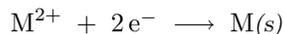
Table 1: Abbreviated table of standard reduction potentials

$\text{Na}^+ + \text{e}^- \rightarrow$	$\text{Na}(s)$	-2.71 v
$\text{Zn}^{2+} + \text{e}^- \rightarrow$	$\text{Zn}(s)$	-.76
$\text{Fe}^{2+} + \text{e}^- \rightarrow$	$\text{Fe}(s)$	-.44
$\text{Cd}^{2+} + \text{e}^- \rightarrow$	$\text{Cd}(s)$	-.40
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow$	$\text{Pb}(s)$	-.126
$2\text{H}^+ + 2\text{e}^- \rightarrow$	$\text{H}_2(g)$	0.000
$\text{AgCl}(s) + \text{e}^- \rightarrow$	$\text{Ag}(s) + \text{Cl}^-(g)$	+ .222
$\text{Hg}_2\text{Cl}_2(s) + 2\text{e}^- \rightarrow$	$2\text{Cl}^-(g) + \text{Hg}(l)$	+ .2676
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow$	$\text{Cu}(s)$	+ .337
$\text{I}_2(s) + 2\text{e}^- \rightarrow$	$2\text{I}^-(s)$	+ .535
$\text{Fe}^{3+} + \text{e}^- \rightarrow$	$\text{Fe}^{2+}(aq)$	+ .771
$\text{Ag}^+ + \text{e}^- \rightarrow$	$\text{Ag}(s)$	+ .799
$\text{O}_2(g) + 4\text{H}^+ + 4\text{e}^- \rightarrow$	$2\text{H}_2\text{O}(l)$	+1.23
$\text{Cl}_2(g) + 2\text{e}^- \rightarrow$	$2\text{Cl}^-(g)$	+1.36

but since the difference $V_{\text{soln}} - V_{\text{Pt}}$ is by definition zero for the hydrogen half-cell, the cell potential we measure corresponds to

$$E_{\text{cell}} = V_{\text{M}} - V_{\text{soln}}$$

which is just the potential of the half-cell



By carrying out a series of measurements in which various other systems are substituted for the M^{2+}/M couple, we can construct a table in which the various half-cell reactions are arranged in order of their potentials. The conventional way of doing this, as shown in Table 3, is to write the half-cell reactions as reductions, and to place them in the order of increasing (more positive) potentials. The resulting values are known as the *standard half-cell potentials*, denoted by E° .

Reference electrodes

In most electrochemical experiments our interested is concentrated on only one of the electrode reactions. Since all measurements must be on a complete cell involving two electrode systems, it is common practice to employ a *reference electrode* as the other half of the cell. The major requirements of a reference electrode is that it be easy to prepare and maintain, and that its potential be

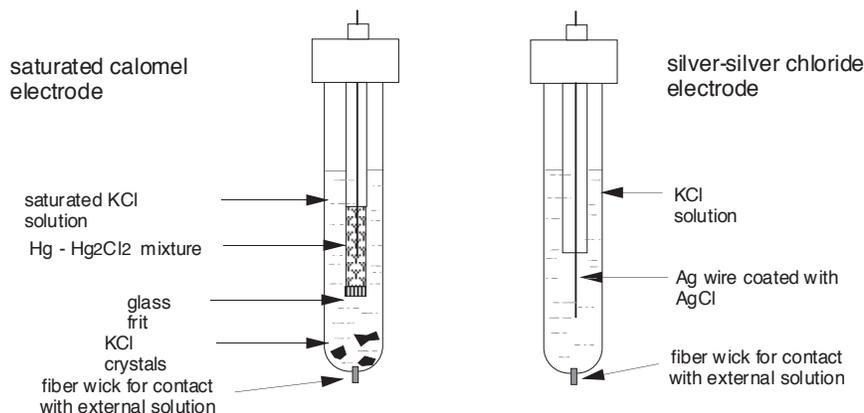


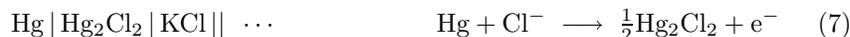
Figure 5: Reference electrodes: the silver-silver chloride and calomel electrodes

stable. The last requirement essentially means that the concentration of any ionic species involved in the electrode reaction must be held at a fixed value. The most common way of accomplishing this is to use an electrode reaction involving a saturated solution of an insoluble salt of the ion. One such system, the *silver-silver chloride electrode* has already been mentioned:



This electrode usually takes the form of a piece of silver wire coated with AgCl. The coating is done by making the silver the anode in an electrolytic cell containing HCl; the Ag^{+} ions combine with Cl^{-} ions as fast as they are formed at the silver surface.

The other common reference electrode is the *calomel electrode*; calomel is the common name for mercury(I) chloride.



The potentials of both of these electrodes have been very accurately determined against the hydrogen electrode. The latter is rarely used in routine electrochemical measurements because it is more difficult to prepare; the platinum surface has to be specially treated by preliminary electrolysis. Also, there is need for a supply of hydrogen gas which makes it somewhat cumbersome and hazardous.

Prediction of cell potentials

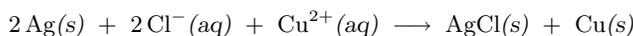
Given the E° values for two half reactions, you can easily predict the potential difference of the corresponding cell: simply add the reduction potential of the reduction half-cell to the *negative* of the reduction potential (that is, to the oxidation potential) of the the oxidation reaction.

Problem Example 2

Find the standard potential of the cell



and predict the direction of electron flow when the two electrodes are connected. *Solution.* The net reaction corresponding to this cell will be



Since this involves the reverse of the AgCl reduction, we must reverse the corresponding half-cell potential:

$$E_{\text{cell}} = (.337 - .222) \text{ v} = .115 \text{ v}$$

Since this potential is positive, then the reaction will proceed to the right, and electrons will be withdrawn from the copper electrode and flow through the external circuit into the silver electrode. Note carefully that in combining these half-cell potentials, we did *not* multiply the E° for the Cu^{2+}/Cu couple by two. The reason for this will be explained later.

Cell potentials and the electromotive series

The remarkable thing about Table 3 is that similar tables, containing the same sequence of reactions, were in common use long before electrochemical cells were studied and half-cell potentials had been measured. If you read down the central column, you will notice that it begins with the sequence of metals Na, Zn, Fe, etc. This sequence is known as the *activity series* of the metals, and expresses the decreasing tendency of the species listed in this column to lose electrons—that is, to undergo oxidation.

The activity series has long been used to predict the direction of oxidation-reduction reactions. Consider, for example, the oxidation of Cu^{2+} by metallic zinc that we have mentioned previously. The fact that zinc is near the top of the activity series means that this metal has a strong tendency to lose electrons. By the same token, the tendency of Zn^{2+} to accept electrons is relatively small. Copper, on the other hand, is a poorer electron donor, and thus its oxidized form, Cu^{2+} , is a fairly good electron acceptor. We would therefore expect the reaction



to proceed in the direction indicated, rather than in the reverse direction. An old-fashioned way of expressing this is to say that “zinc will displace copper from solution”.

The presence of the half-cell potentials in Table 3 allows us to attach numbers to our predictions. As was implied in the preceding problem example, if the

potential of a cell made up of the two half-cell reactions is positive, then the reaction will proceed spontaneously to the right; if it is negative, the *reverse* reaction will be spontaneous.

Cell potentials and free energy

From the above, it should be apparent that the potential difference between the electrodes of a cell is a measure of the tendency for the cell reaction to take place: the more positive the cell potential, the greater the tendency for the reaction to proceed to the right. But we already know that the standard free energy change, ΔG° , expresses the tendency for any kind of process to occur under the conditions of constant temperature and pressure. Thus E° and ΔG° measure the same thing, and are related in a simple way:

$$\boxed{\Delta G^\circ = -n\mathcal{F}E^\circ} \quad (8)$$

A few remarks are in order about this very fundamental and important relation:

- The negative sign on the right indicates that a *positive* cell potential (according to the sign convention discussed previously) implies a *negative* free energy change, and thus that the cell reaction will proceed to the right.
- *Electrical work* is done when an electric charge q moves through a potential difference ΔV . The right side of Eq 8 refers to the movement of n moles of charge across the cell potential E° , and thus has the dimensions of work.
- The Gibbs function is more than a criterion for spontaneity; the value of ΔG° expresses the *maximum useful work* that a system can do on the surroundings. “Useful” here means work other than P - V work that is simply a consequence of volume change, which cannot be channelled to some practical use. This maximum work can only be extracted from the system under the limiting conditions of a reversible change, which for an electrochemical cell, implies zero current. The more rapidly the cell operates, the less electrical work it can supply.
- If \mathcal{F} is expressed in coulombs per mole, the electrical work ΔG° is in joules per mole. To relate these units to electrical units, recall that the coulomb is one amp-sec, and that *power*, which is the *rate* at which work is done, is measured in *watts*, which is the product of amps and volts. Thus

$$1 \text{ J} = 1 \text{ watt-sec} = 1 \text{ (amp-sec)} \times \text{volts}$$

Problem Example 3

For how many minutes could a Cu/Zn cell keep a 100-watt lamp lit, assuming that one mole of reactants are transformed to products, and that the cell voltage is 90 percent of the reversible value E° ?

Solution. From Table 3, E° for the cell



is 1.10 v; 90% of this is 1.0 v. Substituting into Eq 8 with $n = 2$ (two electrons are transferred per mole of reaction), we have

$$-(2 \text{ mol}) \times (96500 \text{ amp-sec mol}^{-1}) \times 1.0 \text{ volt} = -212000 \text{ watt-sec}$$

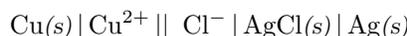
which is also the free energy change under these conditions. The cell can deliver 100 watts for $(212000/100) = 100$ sec, or for about 35 minutes.

If Eq 8 is solved for E° , we have

$$E^\circ = -\frac{\Delta G^\circ}{n\mathcal{F}}$$

This explains why we do not have to multiply the E° s of half reactions by stoichiometric factors when we are finding the E° of a complete cell; since n is in the denominator, we can think of cell potentials as free energy changes *per mole of charge* transferred.

To see this, consider the cell



for which we list the potentials and ΔG° s of the half-reactions:

reaction	E°	$-n\mathcal{F}E^\circ = \Delta G^\circ$
$\text{AgCl}(s) + \text{e}^- \longrightarrow \text{Ag}(s) + \text{Cl}^-$	+ .222 v	-42800 J
$\text{Cu}(s) \longrightarrow \text{Cu}^{2+} + 2\text{e}^-$	- (+.337) v	+65000 J
$2\text{Ag}(s) + 2\text{Cl}^-(\text{aq}) + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{AgCl}(s) + \text{Cu}(s)$	-.115 v	+22200 J

Note, however, that if we are combining two half reactions to obtain a third half reaction, the E° values are *not* additive, since we are not eliminating electrons. Free energies are always additive, so we combine them, and use Eq 8 to find the cell potential.

Problem Example 4

Calculate E° for the electrode Fe^{3+}/Fe from E° values for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Fe^{2+}/Fe .

Solution. Tabulate the E° values and calculate the ΔG° s as follows:

$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$	$E_{o1} = .771 \text{ v}$	$\Delta G^\circ_1 = -.771 \mathcal{F}$
$\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe}(s)$	$E^\circ_2 = -.440 \text{ v}$	$\Delta G^\circ_2 = +.880 \mathcal{F}$
$\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}(s)$	$E^\circ_3 = ?$	$.109 \mathcal{F}$

The free energy for the net half-reaction is $.109n\mathcal{F}$, so $E^\circ_3 = -.109/3 =$
 $-.036 \text{ v}$.

The fall of the electron

A table of standard half-cell potentials such as in Table 3 summarizes a large amount of chemistry, for it expresses the relative powers of various substances to donate and accept electrons by listing reduction half-reactions in order of increasing E° values, and thus of increasing spontaneity. The greater the value of E° , the greater the tendency of the substance on the left to acquire electrons, and thus the stronger this substance is as an oxidizing agent.

One can draw a useful analogy between acid-base and oxidation-reduction reactions. Both involve the transfer of a species from a source, the donor, to a sink, the acceptor. The source and sink nomenclature implies that the tendency of the proton (in the case of acids) or of the electron (for reducing agents) to undergo transfer is proportional to the fall in free energy. From the relation $\Delta G^\circ = -RT \ln K_a$, you can see that the acid dissociation constant is a measure of the fall in free energy of the proton when it is transferred from a donor HA to the solvent H_2O , which represents the reference (zero) free energy level of the proton in aqueous solution.

In the same way, a standard half-cell potential is a measure of the drop in the free energy of the electron when it “falls” from its source level to the energy of the hydrogen ion (at unit effective concentration). By virtue of the defined value of $E^\circ = 0$ for H^+/H_2 , the latter level can also be regarded as the zero free energy level of the electron.

Fig. 6 shows a number of redox couples on an electron free-energy scale. Several conclusions of wide practical importance can be drawn from this table.

- Thus, in Fig. 6 it is seen that Fe^{3+} , representing a rather low-lying empty level, can accept electrons from, and thus oxidize, I^- , $\text{Cu}(s)$, or any higher reductant. Similarly, if Fe^{3+} and I_3^- are both present, one would expect a higher reductant to reduce Fe^{3+} before I_3^- , as long as the two reactions take place at similar rates.
- *Water* can undergo both oxidation and reduction. In the latter role, water can serve as an electron sink to any metal listed above it. These metals are all thermodynamically unstable in the presence of water. A spectacular example of this is the action of water on metallic sodium.
- Water can *donate* electrons to any acceptor *below* it. For example, an aqueous solution of Cl_2 will slowly decompose into hypochlorous acid (HOCl) with the evolution of oxygen.
- Only those substances that appear *between* the two reactions involving water will be stable in aqueous solution in both their oxidized and reduced forms.

This diagram contains the same information as a table of standard potentials, but its different arrangement can provide more insight into the meaning of E° values.

The vertical axis indicates the free energies of electrons when attached to various species, relative to that of the electrons in H_2 . The scale on the left expresses these values as free energies per electron-mole— that is, as conventional E° values. The scale on the right expresses the same thing in terms of kJ.

The chemical species shown on the left are oxidants (oxidizing agents), which can be regarded as substances possessing unoccupied electron energy levels. If an electron donor (a reductant) is added to a solution contain several oxidants, electrons will tend to fall to the lowest empty levels, filling them from the bottom up.

The similarity between this table and a table of proton free energies is striking; just as the pH defines the average proton free energy, and thus controls the ratio of conjugate acid and base species in the solution, so does the E° control the ratio of conjugate oxidant and reductant concentrations.

There is, however, one very important difference: proton-exchange reactions are very fast, but oxidation-reduction reactions can be extremely slow, the order in which a combination oxidants become reduced cannot be predicted from the thermodynamic information given here.

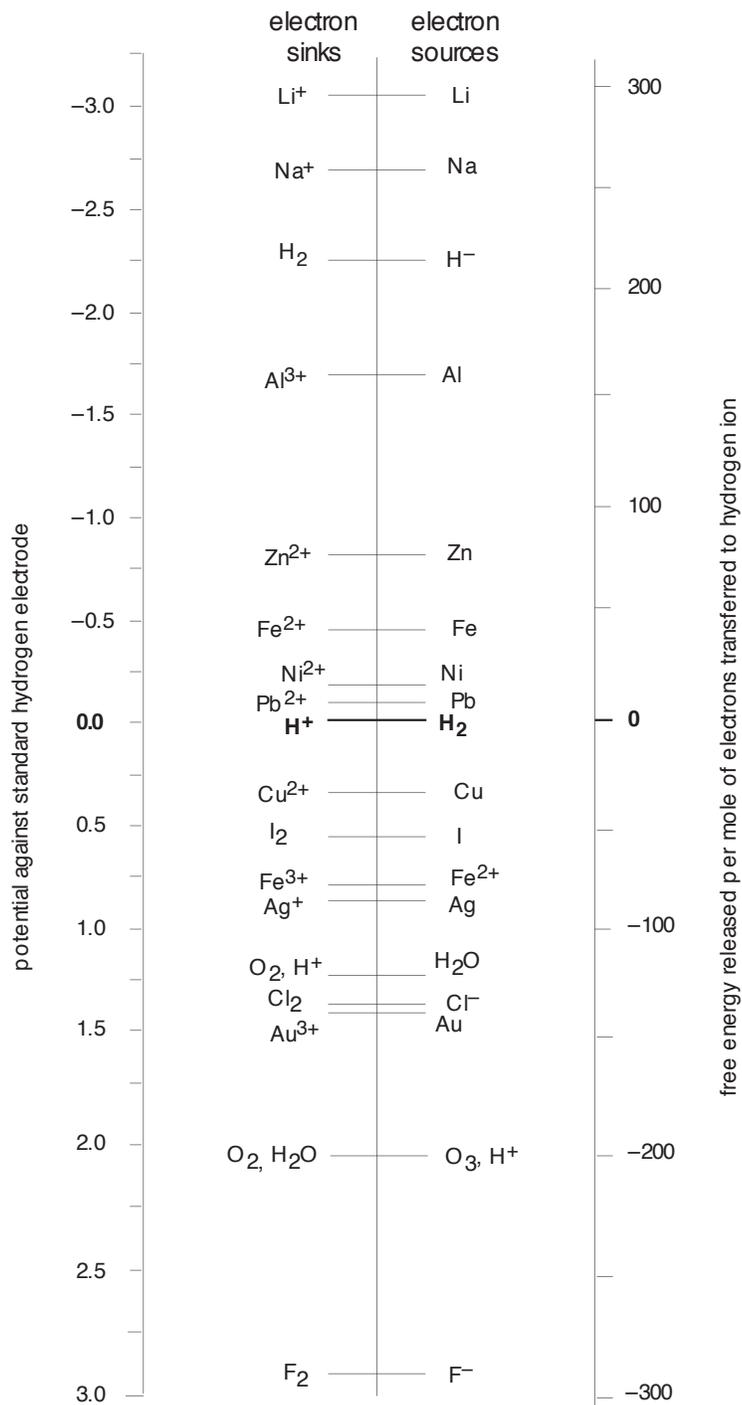


Figure 6: Electron free energy diagram for aqueous solutions.

- A metal that is above the H^+/H_2 couple will react with *acids*, liberating H_2 ; these are sometimes known as the “active” metals. Such metals will also of course react with water.

Latimer diagrams

Considerable insight into the chemistry of a single element can be had by comparing the standard electrode potentials (and thus the relative free energies) of the various oxidation states of the element. The most convenient means of doing this is shown in Fig. 7. The formulas of the species that represent each

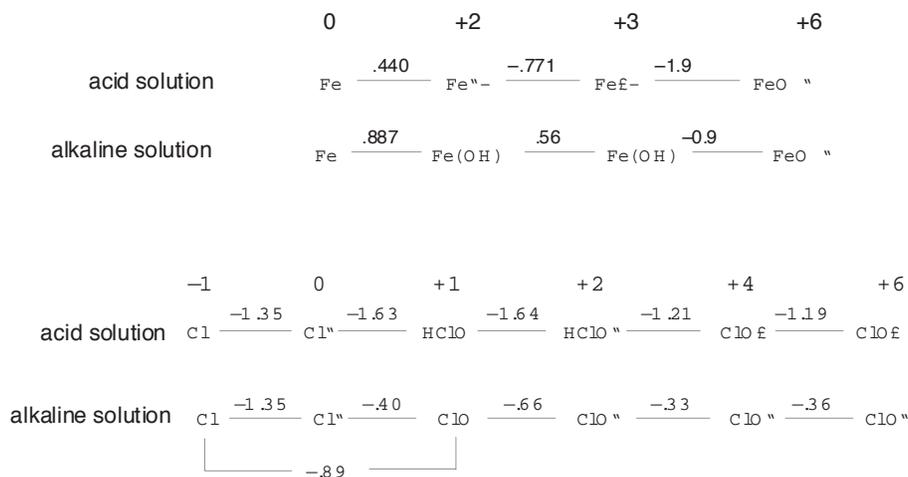


Figure 7: Latimer diagrams showing relative stabilities of different oxidation states of an element

oxidation state of the element are written from left to right in order of increasing oxidation number, and the standard potential for the oxidation of each species to the next on the right is written in between the formulas. (Note that the signs of these potentials are opposite to those in Table 3 because we are writing these as oxidation instead of reduction reactions.) Potentials for reactions involving hydrogen ions will be pH dependent, so separate diagrams are usually provided for acidic and alkaline solutions (effective hydrogen ion concentrations of 1 *M* and 10⁻¹⁴ *M*).

To see how Latimer diagrams are used, look first at the one for iron in acid solution (Fig. 7). The positive value of the Fe/Fe²⁺ potential (.440 v) indicates that Fe will dissolve in 1 *M* H⁺ to form Fe²⁺. Because the oxidation of this species to the +3 state has a negative potential (-.771 v), the +2 state will be the stable oxidation state of iron under these conditions.

An important condition to recognize is when the potential on right of a species is more positive than that on the left. This indicates that the species will tend to undergo *disproportionation*, or self-oxidation and reduction. As an example, consider Cl₂ in alkaline solution. Although the potential for its oxidation is negative, the potential for its *reduction* to Cl⁻ is *positive* (+1.35 v), so

the free energy necessary for the oxidation of one atom of chlorine to hypochlorite can be supplied by the reduction of another to chloride ion. Thus elemental chlorine is thermodynamically unstable with respect to disproportionation in alkaline solution, and the same is true of the oxidation product, HClO^- .

This might be a good time to point out that many oxidation-reduction reactions, unlike most acid-base reactions, tend to be very slow, so the fact that a species is thermodynamically unstable does not always mean that it will quickly decompose. Thus the disproportionation of chlorine mentioned above occurs only very slowly. Interestingly, this process is catalyzed by light, and this is why extra chlorine has to be used to disinfect outdoor swimming pools on sunny days.

4 The Nernst equation

The standard cell potentials we have been discussing refer to cells in which all dissolved substances are at unit activity, which essentially means an “effective concentration” of 1 M . Similarly, any gases that take part in an electrode reaction are at an effective pressure (known as the *fugacity*) of 1 atm. If these concentrations or pressures have other values, the cell potential will change in a manner that can be predicted from the principles you already know.

Suppose, for example, that we reduce the concentration of Zn^{2+} in the Zn/Cu cell from its unit-activity value of around .5 M to a much smaller value:



This will reduce the value of Q for the cell reaction



thus making it more spontaneous, or “driving it to the right” as the Le Châtelier principle would predict, and making its free energy change ΔG more negative than ΔG° , so that E would be more positive than E° .

The relation between the actual cell potential E and the standard potential E° is developed in the following way. First, we can use Eq 8 to express ΔG as well as ΔG° :

$$\Delta G^\circ = -n\mathcal{F}E^\circ \quad (8) \tag{9}$$

$$\Delta G = -n\mathcal{F}E \tag{10}$$

These expressions can then be substituted into the relation

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

which gives

$$-n\mathcal{F}E = -n\mathcal{F}E^\circ + RT \ln Q$$

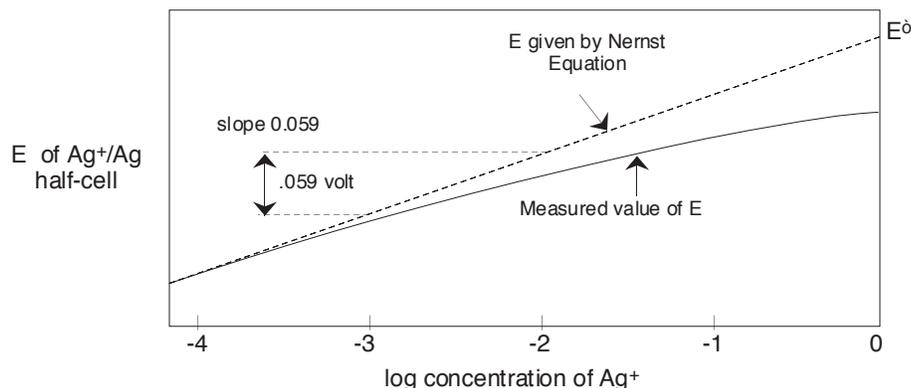


Figure 8: Concentration-dependence of half-cell potentials

which can be rearranged to

$$E = E^\circ - \frac{RT}{n\mathcal{F}} \ln Q \quad (11)$$

This is the very important *Nernst equation* which relates the cell potential to the standard potential E° and to the activities of the electroactive species. Notice that the cell potential will be the same as E° only if Q is unity. The Nernst equation is more commonly written in base-10 log form and for 25°C :

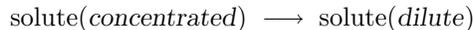
$$E = E^\circ - \frac{.05915}{n} \log Q \quad (12)$$

This relation predicts that a cell potential will change by 59 millivolts per 10-fold change in the concentration of a substance involved in a one-electron oxidation or reduction; for two-electron processes, the variation will be 28 mv per decade concentration change. As illustrated in Fig. 8, these predictions are only fulfilled at low concentrations, not only of the electroactive ion, but of all ionic species. The greater the charge of the ion, the lower the concentration must be.

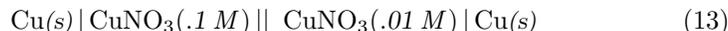
Determination of activity coefficients The activity coefficient γ relates the concentration of an ion to its activity in a given solution: $a = \gamma c$. Since E° s measure activities directly, activity coefficients can be determined by carrying out appropriate EMF measurements on cells in which the concentration of the ion of interest is known. The resulting γ s can then be used to convert concentrations into activities for use in other calculations involving equilibrium constants.

Concentration cells

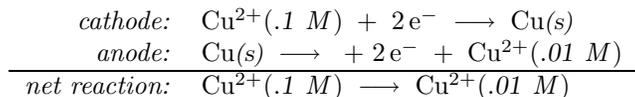
From your study of thermodynamics you may recall that the process



is accompanied by a fall in free energy, and therefore is capable of doing work on the surroundings; all that is required is some practical way of capturing this work. One way of doing this is by means of a *concentration cell* such as



The electrode cell reactions are



which represents the transport of cupric ion from a region of higher concentration to one of lower concentration. The Nernst equation for this cell is

$$E = E^{\circ} - \frac{.05915}{n} \log Q = 0 - .0295 \log .1 = +.0285 \text{ v}$$

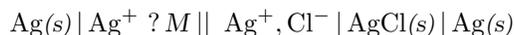
Note that E° for a concentration cell is always zero, since this would be the potential of a cell in which both solutes have the same (standard) effective concentration of unity.

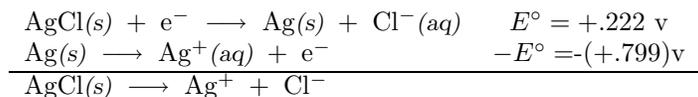
Analytical applications of the Nernst equation

A very large part of Chemistry is concerned, either directly or indirectly, with determining the concentrations of ions in solution. Any method that can accomplish such measurements using relatively simple physical techniques is bound to be widely exploited. Cell potentials are fairly easy to measure, and although the Nernst equation relates them to ionic activities rather than to concentrations, the difference between them becomes negligible in solutions where the total ionic concentration is less than about $10^{-3} M$.

Determination of solubility products

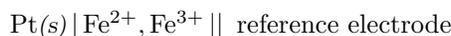
The concentrations of ions in equilibrium with a sparingly soluble salt are sufficiently low that the Nernst equation can be used with little error. Rather than measuring the concentration of the relevant ions directly, the more common procedure is to set up a cell in which one of the electrodes involves the insoluble salt, and whose net cell reaction is just the dissolution of the salt. For example, to determine the K_{sp} for silver chloride, we could use the electrode of Eq 6 in the cell





Potentiometric titrations

In many situations, accurate determination of an ion concentration by direct measurement of a cell potential is impossible due to the presence of other ions and a lack of information about activity coefficients. In such cases it is often possible to determine the ion indirectly by titration with some other ion. For example, the initial concentration of an ion such as Fe^{2+} can be found by titrating with a strong oxidizing agent such as Ce^{4+} . The titration is carried out in one side of a cell whose other half is a reference electrode:



Initially the left cell contains only Fe^{2+} . As the titrant Ce^{4+} is added, the ferrous ion is oxidized to Fe^{3+} in a reaction that is virtually complete:



The cell potential is followed as the Fe^{2+} is added in small increments. Once the first drop of Ce^{3+} has been added, the potential of the left cell is controlled by the ratio of oxidized and reduced iron according to the Nernst equation

$$E = .68 - .059 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

When the equivalence point is reached, the Fe^{2+} will have been totally consumed (the large equilibrium constant ensures that this will be so), and the potential will then be controlled by the concentration ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$. The idea is that *both* species of a redox couple must be present in reasonable concentrations for a concentration to control the potential of an electrode of this kind. If one works out the actual cell potentials for various concentrations of all these species, the resulting titration curve (Fig. 9) looks much like the familiar acid-base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

Measurement of pH

Since pH is actually defined in terms of hydrogen ion *activity* and not its concentration, a hydrogen electrode allows a direct measure of a_{H^+} and thus of $-\log a_{\text{H}^+}$, which is the pH.



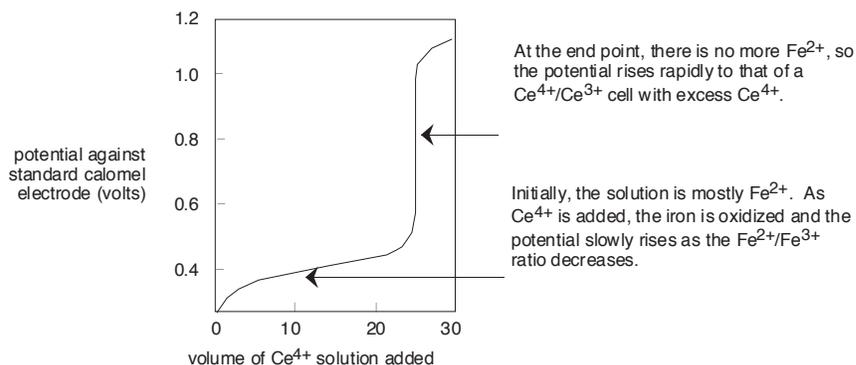
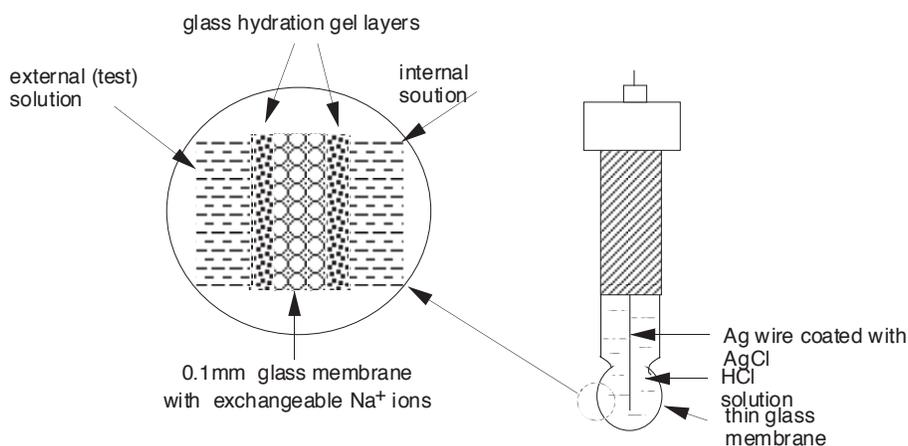
Figure 9: Curve for the potentiometric titration of FeSO_4 with $\text{Ce}(\text{SO}_4)_2$ 

Figure 10: The glass electrode for pH measurements

Although this arrangement (in which the reference electrode could be a standard hydrogen electrode) has been used for high-precision determinations, it would be impractical for routine pH measurements of the kinds that are widely done, especially outside the laboratory.

In 1914 it was discovered that a thin glass membrane enclosing a solution of HCl can produce a potential that varies with $[\text{H}^+]$ in about the same way as that of the hydrogen electrode. Glass electrodes (Fig. 10) are manufactured in huge numbers for both laboratory and field measurements. They contain a built-in Ag-AgCl reference electrode in contact with the HCl solution enclosed by the membrane.

The potential of a glass electrode is given by a form of the Nernst equation very similar to that of an ordinary hydrogen electrode, but of course without

the H_2 :

$$E_{\text{membrane}} = \text{constant} + \frac{RT}{\mathcal{F}} \ln[a_{H^+} + \text{constant}]$$

The reason a glass membrane would behave in this way was not understood until around 1970. It now appears that hydrogen ions in the external solution diffuse through the glass and push out a corresponding number of the Na^+ ions which are normally present in most glasses. These sodium ions diffuse to whichever side of the membrane has the lower H^+ concentration, where they remain mostly confined to the surface of the glass, which has a porous, gelatinous nature. It is the excess charge produced by these positive ions that gives rise to the pH-dependent potential.

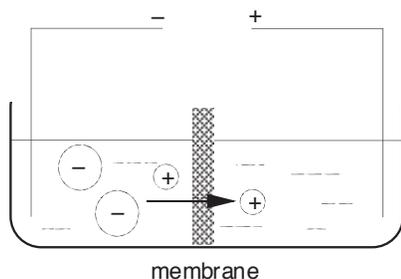
Ion-selective electrodes The function of the membrane in the glass electrode is to allow hydrogen ions to pass through and thus change its potential, while preventing other cations from doing the same thing¹. A glass electrode is thus one form of *ion selective* electrode. Since about 1970, various other membranes have been developed which show similar selectivities to certain other ions. These are widely used in industrial, biochemical, and environmental applications.

Membrane potentials

You may recall the phenomena of osmosis and osmotic pressure that are observed when two solutions having different solute concentrations are separated by a thin film or membrane whose porosity allows small ions and molecules to diffuse through, but which holds back larger particles. If one solution contains a pair of oppositely-charged ionic species whose sizes are very different, the smaller ions may pass through the semipermeable membrane while the larger ones are retained. This will produce a charge imbalance between the two solutions, with the original solution having the charge sign of the larger ion. Eventually the electrical work required to bring about further separation of charges becomes too large to allow any further net diffusion to take place, and the system settles into an equilibrium state in which a constant potential difference (usually around a volt or less) is maintained. This potential difference is usually called a *membrane potential* or *Donnan potential*.

Fig. 11 shows a simple system containing the potassium salt of a protein on one side of a membrane, and potassium chloride on the other. The proteinate anion, being too large to diffuse through the membrane, gives rise to the potential difference. The value of this potential difference can be expressed by a

¹This selectivity is never perfect; most glass electrodes will respond to moderate concentrations of sodium ions, and to high concentrations of some others.



If the smaller ions are able to diffuse through the membrane but the larger ones cannot, a potential difference will develop between the two solutions. This membrane potential can be observed by introducing a pair of Pt electrodes.

Figure 11: Origin of a membrane potential

relation that is essentially the same as the Nernst equation, although its derivation is different. The membrane potential can be expressed in terms of the ratio of either the K^+ or Cl^- ion activities:

$$\Delta\Phi = \frac{RT}{n\mathcal{F}} \ln \frac{\{K^+\}_{\text{right}}}{\{K^+\}_{\text{left}}} = \frac{RT}{n\mathcal{F}} \ln \frac{\{Cl^-\}_{\text{left}}}{\{Cl^-\}_{\text{right}}} \quad (14)$$

The membrane surrounding most living cells contains sites or “channels” through which K^+ ions are selectively transported so that the concentration of K^+ inside the cell is 10-30 times that of the intracellular fluid. Taking the activity ratio as about 20, Eq 14 predicts that the potential difference $\phi_{\text{inside}} - \phi_{\text{outside}}$ will be

$$\Delta\Phi = .059 \log_{10} \frac{1}{20} = -70 \text{ mV}$$

which is consistent with observed values. Transport of an ion such as K^+ from a region of low concentration into the more concentrated intercellular fluid requires a source of free energy, which is supplied by ATP under enzymatic control. The metabolic processes governing this action are often referred to as “ion pumps”.

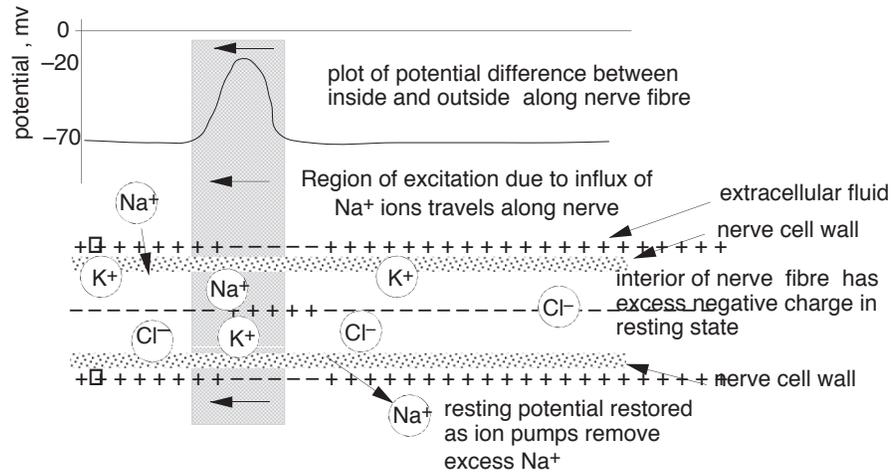


Figure 12: Conduction of nerve impulses

Nerve conduction Transmission of signals through the nervous system occurs not by the movement of a charge carrier through the nerve, but by waves of varying ion pump activity that travel along the length of the nerve.

The normal potential difference between the inner and outer parts of nerve cells is about -70 mv as estimated above. Transmission of a nerve impulse is initiated by a lowering of this potential difference to about -20 mv. This has the effect of temporarily opening the Na^+ channel; the influx of these ions causes the membrane potential of the adjacent portion of the nerve to collapse, leading to an effect that is transmitted along the length of the nerve. As this pulse passes, K^+ and Na^+ pumps restore the nerve to its resting condition.

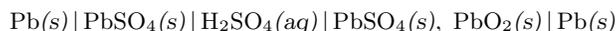
5 Batteries and fuel cells

An electrochemical cell which operates spontaneously can deliver an amount of work to the surroundings whose upper limit (in the case of reversible operation) is equal to the fall in free energy as the cell reaction proceeds. In the process, chemical energy is converted into electrical energy, which may in turn be utilized in a variety of practical ways. As the reaction continues the free energy of the system falls, so as time goes by less energy remains to be recovered. Eventually the cell reaction comes to equilibrium ($\Delta G = 0$) and no further work can be extracted; the cell is “dead”.

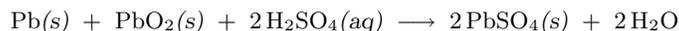
A *battery* is a practical adaptation of this arrangement and usually consists of a number of cells connected in series so as to attain the desired output voltage. One of the earliest batteries was based on the simple zinc-copper cell of Fig. 2; this was used, among other things, for telegraphy and railroad signalling during the nineteenth century, when batteries provided the only practical source of electrical power.

Batteries are usually classified as *primary* or *secondary* cells. The latter is also called a *storage cell*, which more aptly describes its ability to convert electrical energy into chemical energy and then re-supply it as electrical energy on demand. The cell reaction of a storage cell can proceed in either direction; during charging, electrical work is done on the cell to provide the free energy needed to force the reaction in the non-spontaneous direction. A primary cell, as exemplified by an ordinary flashlight battery, cannot be recharged with any efficiency, so the amount of energy it can deliver is limited to that obtainable from the reactants that were placed in it at the time of manufacture.

The most well-known storage cell is the lead-acid cell, which was invented by Planté in 1859 and is still the most practical known way of storing large quantities of electrical energy. The cell is represented by



and the net cell reaction



The reaction proceeds to the right during discharge and to the left during charging. The state of charge can be estimated by measuring the density of the electrolyte; sulfuric acid is about twice as dense as water, so as the cell is discharged, the density of the electrolyte decreases.

The fuel cell

Conventional batteries supply electrical energy from the chemical reactants stored within them; when these reactants are consumed, the battery is “dead”. An alternative approach would be to feed the reactants into the cell as they

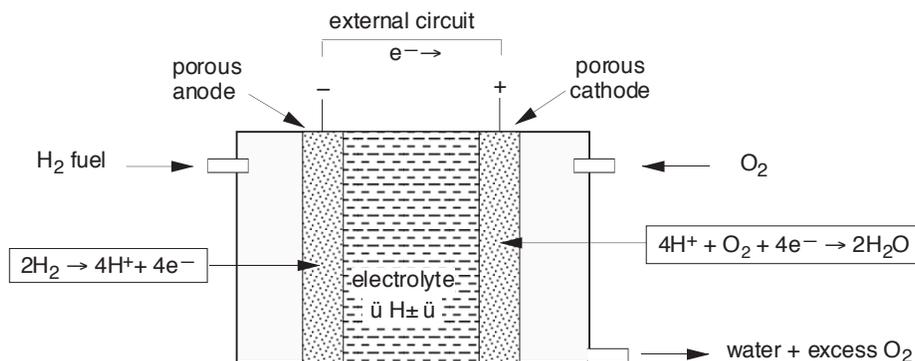
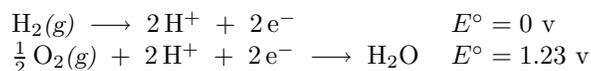


Figure 13: The hydrogen-oxygen fuel cell

are required, so as to permit the cell to operate continuously. In this case the reactants can be thought of as “fuel” to drive the cell, hence the term *fuel cell*.

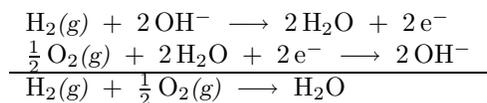
Although fuel cells were not employed for practical purposes until space exploration began in the 1960's, the principle was first demonstrated in 1839 by Sir William Grove, a lawyer and amateur chemist. At the time, it was already known that water could be decomposed into hydrogen and oxygen by electrolysis; Grove tried recombining the two gases in a simple apparatus, and discovered what he called “reverse electrolysis”:



The overall reaction is just the formation of water from its elements



It was not until 1959 that the first working hydrogen-oxygen fuel cell was developed. Modern cells employ an alkaline electrolyte, so the electrode reactions differ from the one shown above by the addition of OH⁻ to both sides of the equations (note that the net reaction is the same):



In place of dihydrogen, other fuels such as alcohols, hydrocarbon liquids, and even coal slurries have been used; methanol appears to be an especially promising fuel.

One reason for the interest in fuel cells is that they offer a far more efficient way of utilizing chemical energy than does conventional thermal conversion.

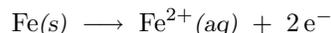
The work obtainable from Eq 15 in the limit of reversible operation of a fuel cell is 229 kJ per mole of H₂O formed. If the hydrogen were simply burned in oxygen, the heat obtainable would be $-\Delta H^\circ = 242 \text{ kJ mol}^{-1}$, but no more than about half of this heat can be converted into work², so the output would be 121 kJ mol⁻¹ or less.

The major limitation of present fuel cells is that the *rates* of the electrode reactions, especially the one in which oxygen is reduced, tend to be very small, and thus so is the output current per unit of electrode surface. Coating the electrode with a suitable catalytic material is almost always necessary to obtain useable output currents, but good catalysts are mostly very expensive substances such as platinum, so that the resulting cells are too costly for most practical uses. There is no doubt that if an efficient, low-cost catalytic electrode surface is ever developed, the fuel cell would become a mainstay of the energy economy.

6 Electrochemical Corrosion

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Under normal environmental conditions, the thermodynamically stable states of most of the metallic elements are the cations, rather than the metal itself. This is the reason that considerable energy (and expense) must go into the extraction of a metal from its ore. However, once the metal is won and put into use, it tends to spontaneously revert back to its more stable form. To do so, the metal must lose electrons, and this requires the presence of an electron acceptor or oxidizing agent. Dioxygen, of course, is the most prominent of these, but hydrogen ions and the cations of any more “noble” metal³.

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. In this sense the system can be regarded as an electrochemical cell in which the anodic process is something like



and the cathodic steps can be any of



²This limit is a consequence of the Second Law of Thermodynamics. The fraction of heat that can be converted into work is a function how far (in temperature) the heat falls as it flows through the engine and into the surroundings. $\epsilon = (1 - T_{\text{high}})/T_{\text{low}}$. At normal environmental temperatures of around 300 °K, T_{high} would have to be at least 600 °K for 50% thermal efficiency.

³A *noble* metal is one that appears toward the bottom of a listing of standard reduction potentials as in Table 3. From Fig. 6, you can see that such metals serve as lower-free energy sinks which can accept electrons from higher (less noble) metals.

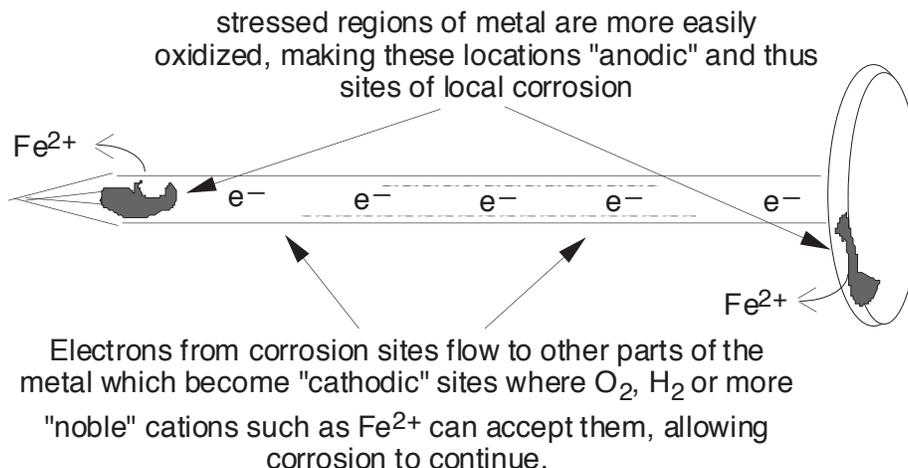
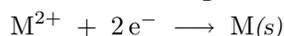
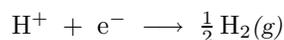


Figure 14: Electrochemical corrosion of a nail showing anodic and cathodic regions



where M is an more noble metal. A thin film of moisture on the surface of the metal can serve as the medium for the electrolyte.

Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic, as shown on the nail in Fig. 14.

For part of a metal to act as the site for oxidation and dissolution, it must be in contact with the electrolyte, which may be no more than a film of adsorbed moisture. However, practically all metallic surfaces that have been exposed to the atmosphere are coated with a thin film of the metal oxide, which tends to shield the metal from the electrolyte and thus prevent corrosion⁴. If one part of a metallic object is protected from the atmosphere so that there is insufficient O_2 to build or maintain the oxide film, this "protected" region will often be the site at which corrosion is most active. The fact that such sites are usually hidden from view accounts for much of the difficulty in detecting and controlling corrosion.

In contrast to anodic sites, which tend to be localized to specific regions of the surface, the cathodic part of the process can occur almost anywhere.

⁴Metals such as aluminum and stainless steels form extremely tough and adherent oxide films that afford extraordinary corrosion resistance.

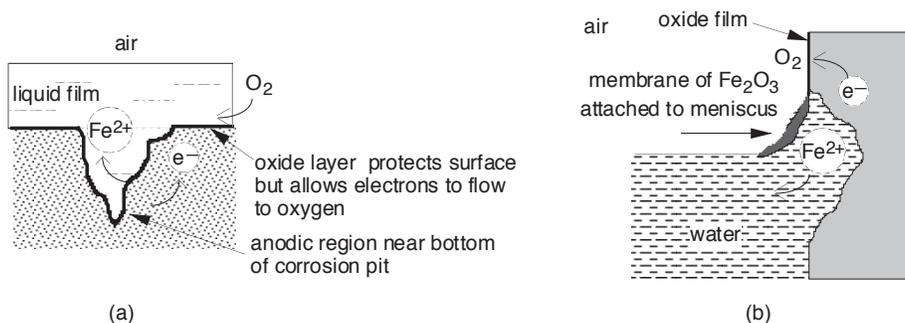


Figure 15: Corrosion in oxygen-deprived regions at pitting and immersion locations

Because metallic oxides are usually semiconductors, most oxide coatings do not inhibit the flow of electrons to the surface, so almost any region that is exposed to O_2 or to some other electron acceptor can act as a cathode.

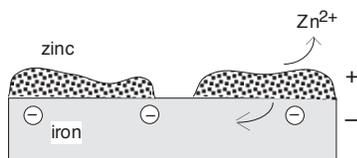
The tendency of oxygen-deprived locations to become anodic is the cause of many commonly-observed patterns of corrosion. Thus *pitting corrosion* (Fig. 15a) begins when corrosion hollows out a narrow hole, or pit, in the metal. The bottoms of these pits tend to be deprived of oxygen, thus promoting further growth of the pit into the metal. Fig. 15b shows how corrosion of a metal that is partially immersed in water is often concentrated at the water line.

Rusted-out cars and bathroom stains. Anyone who has owned an older car has seen corrosion occur at joints between body parts and under paint films. You will also have noticed that once corrosion starts, it tends to feed on itself. One reason for this is that one of the products of the O_2 reduction reaction is hydroxide ion. The high pH produced in these cathodic regions tends to destroy the protective oxide film, and may even soften or weaken paint films, so that these sites can become anodic. The greater supply of electrons promotes more intense cathodic action, which spawns even more anodic sites, and so on.

A very common cause of corrosion is having two dissimilar metals in contact, as might occur near a fastener or at a weld joint. Moisture collects at the junction point, acting as an electrolyte and forming a cell in which the two metals serve as electrodes. Moisture and conductive salts on the outside surfaces acts as an external conductor, effectively short-circuiting the cell and producing very rapid corrosion; this is why cars rust out so quickly in places where salt is placed on roads to melt ice.

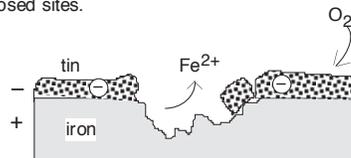
Dissimilar-metal corrosion can occur even if the two metals are not initially in direct contact. For example, in homes where copper tubing is used for plumbing, there is always a small amount of dissolved Cu^{2+} in the water. When this water encounters steel piping or a chrome-plated bathroom sink drain, the more-noble copper will plate out on the other metal, producing a new metals-in-contact corrosion cell. In the case of chrome bathroom sink fittings, this leads to the formation of Cr^{3+} salts which precipitate as greenish stains.

Sacrificial coating of more active metal protects exposed area of base by supplying electrons, keeping it cathodic.



(a) Galvanized iron

A noble coating such as tin will withdraw electrons from base metal, thus forcing it anodic and actually promoting corrosion at exposed sites.



(b) Tin can

Figure 16: Corrosion protection by sacrificial coating, and its reverse

Control of corrosion

Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of only one will stop corrosion. The most obvious strategy is to stop both processes by coating the object with a paint or other protective coating. Even if this is done, there are likely to be places where the coating is broken or does not penetrate, particularly if there are holes or screw threads.

A more sophisticated strategy is to maintain a continual negative electrical charge on a metal, so that its dissolution as positive ions is inhibited. Since the entire surface is forced into the cathodic condition, this method is known as *cathodic protection*. The source of electrons can be an external direct current power supply (commonly used to protect oil pipelines and other buried structures), or it can be the corrosion of another, more active metal. The most common example of the latter is the zinc-coating on galvanized steel, illustrated in Fig. 16a. The zinc coating, being less noble than iron, tends to corrode selectively. Dissolution of this *sacrificial coating* leaves behind electrons which concentrate in the iron, making it cathodic and thus inhibiting its dissolution.

The effect of plating iron with a *less* active metal provides an interesting contrast. The common tin-plated can (Fig. 16b) is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the iron more anodic so now the tin is actively promoting corrosion of the iron! You have probably observed how tin cans disintegrate very rapidly when left outdoors.

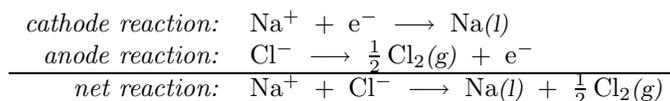
7 Electrolytic cells

Electrolysis refers to the decomposition of a substance by an electric current. The electrolysis of sodium and potassium hydroxides, first carried out in 1808 by Sir Humphrey Davey, led to the discovery of the two metallic elements and

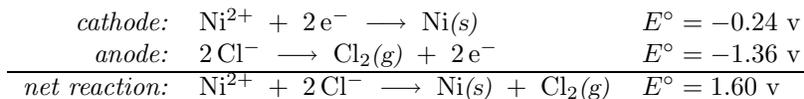
showed that these two hydroxides which had previously been considered undecomposable and thus elements, were in fact compounds:

“By means of a flame which was thrown on a spoon containing potash, this alkali was kept for some minutes at a strong red heat, and in a state of perfect fluidity.” One pole of a battery of copper-zinc cells was connected to the spoon, and the other was connected to platinum wire which dipped into the melt. *“By this arrangement some brilliant phenomena were produced. The potash appeared to be a conductor in a high degree, and as long as the communication was preserved, a most intense light was exhibited at the negative wire, and a column of flame, which seemed to be owing to the development of combustible matter, arose from the point of contact.”* The flame was due to the combustion in the air of metallic potassium. In another experiment, Davy observed *“small globules having a high metallic lustre, precisely similar in visible characters to quicksilver, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces.”*

Electrolysis of molten alkali halides is the usual industrial method of preparing the alkali metals:



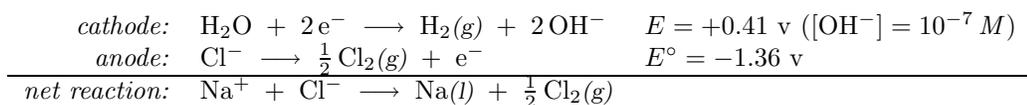
Ions in aqueous solutions can undergo similar reactions. Thus if a solution of nickel chloride undergoes electrolysis at platinum electrodes, the reactions are



Both of these processes are carried out in electrochemical cells which are forced to operate in the “reverse”, or non-spontaneous direction, as indicated by the negative E° for the above cell reaction. The free energy is supplied in the form of electrical work done on the system by the outside world (the surroundings). This is the only fundamental difference between an *electrolytic* cell and the *galvanic cell* in which the free energy supplied by the cell reaction is extracted as work done on the surroundings.

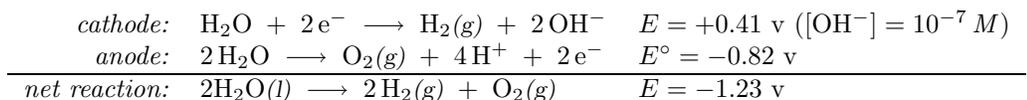
Electrolysis involving water

If we substitute sodium chloride for nickel chloride, dihydrogen is produced at the cathode instead of sodium:



The reason that sodium is not a product of this reaction is best understood by locating the couples Na^+/Na and $\text{H}_2\text{O}/\text{H}_2, \text{OH}^-$ in Fig. 6 or Table 3. Reduction of Na^+ ($E^\circ = 2.7 \text{ v}$) is energetically more difficult than the reduction of water, so in aqueous solution the latter will prevail.

You will recall that water can be oxidized as well as reduced, so if we replace the chloride ion with an anion such as nitrate or sulfate that is much more difficult to oxidize, the water is oxidized instead. Electrolysis of a solution of sulfuric acid or of a salt such as NaNO_3 results in the decomposition of water at both electrodes:



Faraday's laws of electrolysis

One mole of electric charge (96,500 coulombs), when passed through a cell, will discharge *half* a mole of a divalent metal ion such as Cu^{2+} . This relation was first formulated by Faraday in 1832 in the form of two *laws of electrolysis*:

1. The weights of substances formed at an electrode during electrolysis are directly proportional to the quantity of electricity that passes through the electrolyte.
2. The weights of different substances formed by the passage of the same quantity of electricity are proportional to the equivalent weight of each substance.

The *equivalent weight* of a substance is defined as the molar mass, divided by the number of electrons required to oxidize or reduce each unit of the substance. Thus one mole of V^{3+} corresponds to three equivalents of this species, and will require three faradays of charge to deposit it as metallic vanadium.

Now that we have a good understanding of electrolytes and electrolysis, the quantitative treatment of electrolytic reactions can be handled by ordinary chemical stoichiometry as in the Problem Example on page 6, so explicit use of Faraday's laws is not usually necessary.

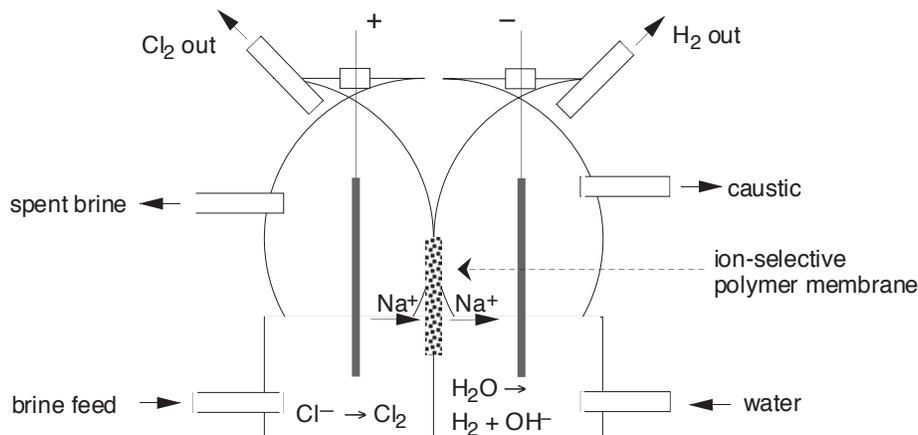


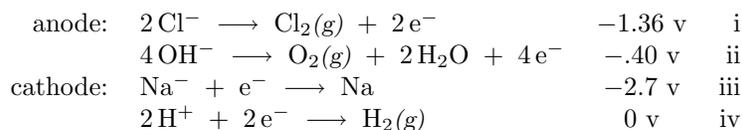
Figure 17: Membrane cell for industrial chloralkali production

Industrial electrolytic processes

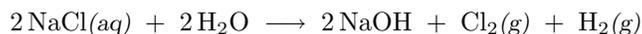
For many industrial-scale operations involving the oxidation or reduction of both inorganic and organic substances, and especially for the production of the more active metals such as sodium, calcium, magnesium, and aluminum, the most cost-effective reducing agent is electrons supplied by an external power source. The two most economically important of these processes are described below.

The chloralkali industry.

The electrolysis of brine is carried out on a huge scale for the industrial production of chlorine and caustic soda (sodium hydroxide). Because the reduction potential of Na^+ is much higher than that of water, the latter substance undergoes decomposition at the cathode, yielding hydrogen gas and OH^- .



A comparison of the E° s would lead us to predict that reactions (ii) and (iv) would predominate and that (iii) would be unimportant. It is true that sodium ion is not reduced, but as was mentioned in the section on fuel cells, electrode reactions involving O_2 are notoriously slow, so even though it is less favored thermodynamically, reaction (i) predominates over (ii). The net reaction for the chlorination of brine is thus



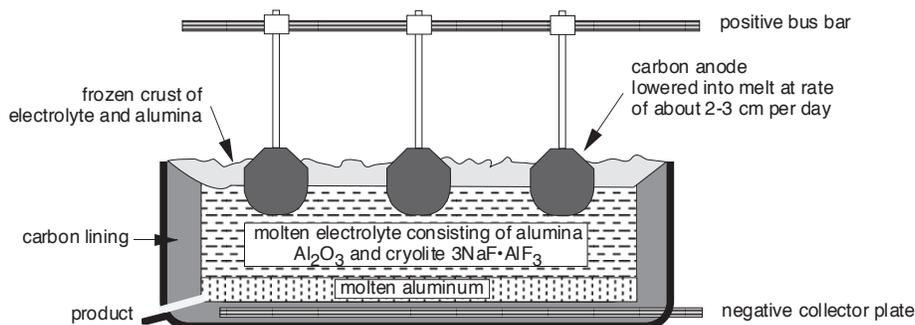


Figure 18: Hall-Héroult cell for the production of aluminum

Since chlorine reacts with both OH^- and H_2 , it is necessary to physically separate the anode and cathode compartments. In modern plants this is accomplished by means of an ion-selective polymer membrane, but prior to 1970 a more complicated cell was used that employed a pool of mercury as the cathode. A small amount of this mercury would normally find its way into the plant's waste stream, and this has resulted serious pollution of many major river systems and estuaries and devastation of their fisheries. Even though these mercury cells have now mostly been removed, the aquatic pollution will continue for hundreds of years as the mercury is slowly released from bottom sediments.

Electrolytic refining of aluminum

Aluminum is present in most rocks, makes up 8% of the earth's crust, and is potentially the world's most abundant metal. Its isolation, however, is very difficult to accomplish by purely chemical means, as evidenced by the high E° of the Al^{3+}/Al couple. For the same reason, aluminum cannot be isolated by electrolysis of aqueous solutions of its compounds, since the water would be electrolyzed preferentially. And if you have ever tried to melt a rock, you will appreciate the difficulty of electrolyzing a molten aluminum ore! Aluminum was in fact considered an exotic and costly metal until 1886, when Charles Hall (U.S.A) and Paul Héroult (France) independently developed a practical electrolytic reduction process.

The Hall-Héroult process takes advantage of the principle that the melting point of a substance is reduced by admixture with another substance with which it forms a homogeneous phase. Instead of using the pure alumina ore Al_2O_3 which melts at 2050°C , it is mixed with *cryolite*, which is a natural mixture of NaF and AlF_3 , thus reducing the temperature required to a more manageable 1000°C . The anodes of the cell are made of carbon (actually a mixture of pitch and coal), and this plays a direct role in the process; the carbon gets

oxidized (by the oxide ions left over from the reduction of Al^{3+}) to CO, and the free energy of this reaction helps drive the aluminum reduction, lowering the voltage that must be applied and thus reducing the power consumption. This is important, because aluminum refining is the largest consumer of industrial electricity, accounting for about 5% of all electricity generated in North America. Since aluminum cells commonly operate at about 100,000 amperes, even a slight reduction in voltage can result in a large saving of power.

The net reaction is



However, large quantities of CO and of HF (from the cryolite), and hydrocarbons (from the electrodes) are formed in various side reactions, and these can be serious sources of environmental pollution.