

Electrochemistry

Chemical reactions at an electrode, galvanic and electrolytic cells

A Chem 1 Reference Text

Stephen K. Lower • Simon Fraser University¹

Table of contents

1: Chemistry and electricity	3
Electroneutrality	3
Potential differences at interfaces	5
2: Electrochemical cells	6
Transport of charge within the cell	7
Cell description conventions	8
Electrodes and electrode reactions	8
Standard half-cell potentials	9
Reference electrodes	11
3: Prediction and significance of cell potentials	12
Cell potentials and the electromotive series	13
Cell potentials and free energy	13
4: The Nernst equation	18
Concentration cells	23
Thermodynamics of galvanic cells	23
Analytical applications of the Nernst equation	23
Membrane potentials	27
5: Batteries and fuel cells	28
The ideal and the real	28
Primary and secondary batteries	29
Timeline of battery development	30
The fuel cell	31
6: Electrochemical Corrosion	32
7: Electrolytic cells	35
Electrolysis in aqueous solutions	36
Faraday's laws of electrolysis	37
Industrial electrolytic processes	38

1. To contact the author, please use the Web form at http://www.chem1.com/VT_mail.html



Chem 1
Virtual Textbook
reference text

The Chem I Virtual Textbook is a collection of reference textbook chapters and tutorial units providing in-depth coverage of topics in college-level General Chemistry.

For a more information on the Virtual Textbook contents, see
<http://www.chem1.com/acad/webtext/virtualtextbook.html>

This document covers Electrochemistry at a level appropriate for first-year college chemistry.
It was last modified on 23 September 2004 .

It can be downloaded from <http://www.chem1.com/acad/pdf/elchem.pdf>

A Web-based version is available at <http://www.chem1.com/acad/webtext/elchem/>.

1 • Chemistry and electricity

The connection between chemistry and electricity is a very old one, going back to ALESSANDRO 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 “travelers”). 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.

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 DAVEY prepared the first elemental sodium by electrolysis of a sodium hydroxide melt. It was left to Davey's former assistant, MICHAEL FARADAY, to show that there is a direct relation between the amount of electric charge passed through the solution and the quantity of electrolysis products. 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.

1.1 Electroneutrality

Nature seems to 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 within the metal 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 still too low (around $10^{-10} M$) to be detected by ordinary chemical means.

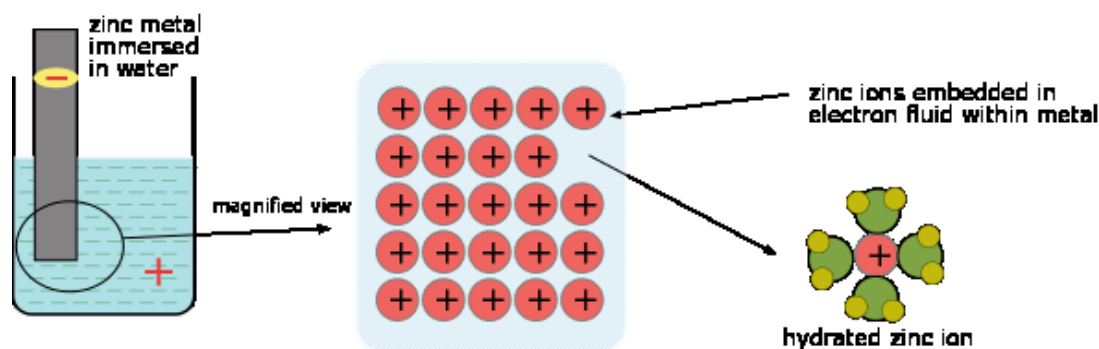


Fig. 1: Oxidation of metallic zinc in contact with water

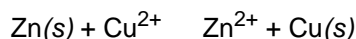
There would be no build-up of opposing charges in the two phases if the excess electrons could be removed from the metal or the positive ions consumed as the reaction proceeds. For example, we could drain off the electrons left behind in the zinc through an external circuit that forms part of a complete 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, water itself 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 unbalances in the concentrations of oppositely charged particles that are not chemically significant. 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 of the process, making it less spontaneous.

The only way we can get the oxidation of the metal 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 to 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 ion introduced to the solution, one Cu ion is removed. The net reaction



quickly goes to completion.

1.2 Potential differences at interfaces

The transition region between two phases consists of a region of charge unbalance known as the *electric double layer*. As its name implies, this consists of an inner monomolecular layer of adsorbed water molecules and ions, and an outer diffuse region that compensates for any local charge unbalance that gradually merges into the completely random arrangement of the bulk solution. In the case of a metal immersed in pure water, the electron fluid within the metal causes the polar water molecules to adsorb to the surface and orient themselves so as to create two thin planes of positive and negative charge. If the water contains dissolved ions, some of the larger (and more polarizable) anions will loosely bond (*chemisorb*) to the metal, creating a negative inner layer which is compensated by an excess of cations in the outer layer.

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 can always be represented as a chemical reaction and is known generally as an **electrode process**. Electrode processes take place within the double layer and produce a slight unbalance in the electric charges of the electrode and the solution. 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, 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 until you consider that this potential difference spans a very small distance. 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. Thus a very small voltage can produce a very large potential *gradient*. For example, a potential difference of one volt across a typical 10^{-8} cm interfacial boundary amounts to a potential gradient of 100 million volts per centimeter— a very significant value indeed!

Interfacial potentials are not confined to metallic electrodes immersed in solutions; they can in fact 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.

Interfacial potential differences are not directly observable. The usual way of measuring a potential difference between two points is to bring the two leads of a voltmeter into contact with them. It's simple enough to touch one lead of the meter to a metallic electrode, but there is no way you can connect the other lead to the solution side of the interfacial region without introducing a second electrode with its own interfacial potential, so you would be measuring the sum of *two* potential differences. Thus *single electrode potentials*, as they are commonly known, are not directly observable.

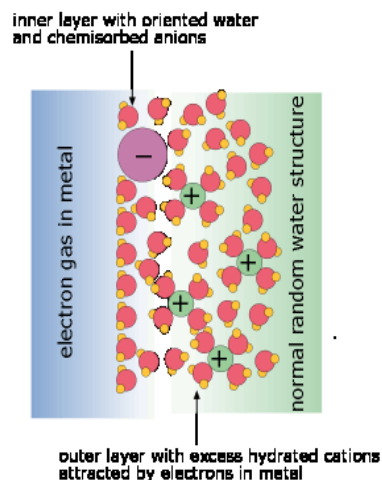


Fig. 2: Electric double layer at an electrode surface

2 • Electrochemical cells

Although it is physically impossible to measure or manipulate the potential difference between a piece of metal and the solution in which it is immersed, we can easily measure a potential difference between two such electrodes immersed in a solution. The result will be the sum of the two electrode potentials, we shall see farther on that such measurements can supply all the information we need in order to characterize the two electrode reactions.

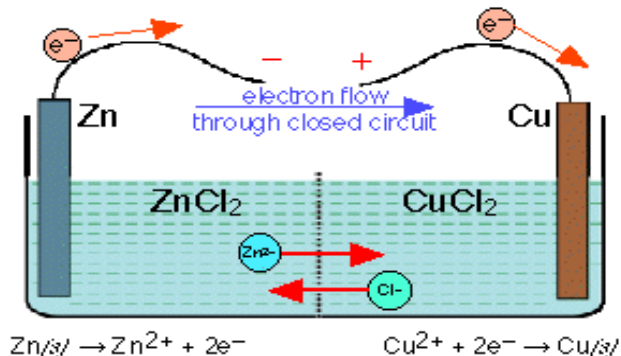


Fig. 3: A simple electrochemical cell

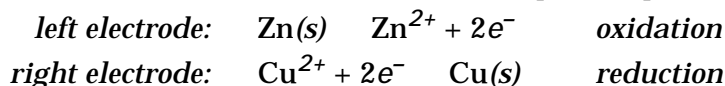
The two compartments of this cell are separated by a porous barrier that allows ions to pass through while preventing gross mixing of the two solutions. When the two electrodes are connected, charges flow in the directions indicated. Note that the buildup of positive charge on the left side can be offset either by diffusion of Zn^{2+} to the right or (less efficiently) by Cl^{-} to the left.

This 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. The two solutions are separated by a porous barrier that prevents them from rapidly mixing but allows ions to diffuse through.

If we simply left it at that, 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 which become “discharged”, that is, converted into Cu atoms at the surface of the copper electrode. The net reaction is the same as before—the oxidation of zinc by copper(II) ions:



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



Electrochemical cells allow measurement and control of a redox reaction. The reaction can be started and stopped by connecting or disconnecting the two electrodes. If we place a variable resistance in the circuit, we can even control the rate of the net cell reaction by simply turning a knob. By connecting a battery or other source of current to the two electrodes, we can 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 F . Careful experiments have determined that $1 F = 96467 \text{ c}$. For most purposes, you can simply use 96,500 coulombs 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. 3, 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

$$(0.15 \text{ amp}) \times (54600 \text{ sec}) = 810 \text{ c}$$

or

$$(810 \text{ c}) / (96500 \text{ c } F^{-1}) = 0.0084 F$$

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 $(.0043 \text{ mol}) \times (65.37 \text{ g mol}^{-1}) = 0.275 \text{ g}$

2.1 Transport of charge within the cell

In order for the cell of Fig. 3 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, causing the solution in contact with the zinc to acquire a net positive charge, while a net negative charge would build up in the solution on the copper side of the cell. These violations of electroneutrality would make it more difficult (require more work) to introduce additional Zn^{2+} ions into the positively-charged electrolyte or for electrons to flow into right compartment where they are needed to reduce the Cu^{2+} ions, thus effectively stopping the reaction after only a minute amount has taken place.

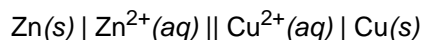
In order to sustain the cell reaction, the charge carried by the electrons through the external circuit must be accompanied by a compensating transport of ions between the two cells. This means that we must provide a path for ions to move directly from one cell to the other. This ionic transport involves 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 intermediate compartment 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.

2.2 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? 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. 3.

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

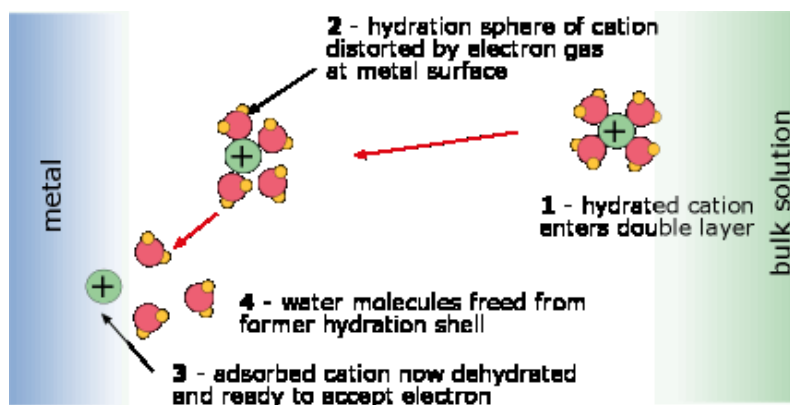
- The **anode** is where oxidation occurs, and the **cathode** is the site of reduction. In an actual cell, either electrode can have either identity, depending on the direction in which the net cell reaction is occurring.
- If electrons flow from the left electrode to the right electrode (as depicted in the above cell notation) 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.

2.3 Electrodes and electrode reactions

The electron-transfer step that takes place at each electrode is known as the *electrode reaction*. The substances that receive and lose electrons are called the **electroactive species**.

Fig. 4: Electron transfer at an electrode

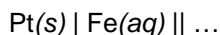
This process takes place within the very thin interfacial region at the electrode surface, and involves quantum-mechanical tunneling of electrons between the electrode and the electroactive species. The work required to displace the H₂O molecules in the hydration spheres of the ions constitutes part of the activation energy of the process.



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.

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



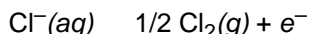
and the half-cell reaction would be



The reaction occurs at the surface of the electrode (Fig?). 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 is always endothermic, sometimes to such an extent that only a small fraction of the ions be able to contact the surface closely 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 an electrochemically inert conductor such as platinum. A typical reaction of considerable commercial importance is



Similar reactions involving the oxidation of Br_2 or I_2 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



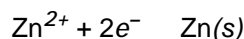
Although the usefulness of such an electrode may not be immediately apparent, this kind of electrode finds very wide application in electrochemical measurements, as we shall see later.

2.4 Standard half-cell potentials

When a net reaction proceeds in an electrochemical cell, oxidation occurs at one electrode (the anode) and reduction takes place at the other electrode (the cathode.) We can think of the cell as consisting of two *half-cells* joined together by an external circuit through which electrons flow and an internal pathway that allows ions to migrate between them so as to preserve electroneutrality.

Reduction potentials Each half-cell has associated with it a potential difference whose magnitude depends on the nature of the particular electrode reaction and on the concentrations of the dissolved electroactive species. The *sign* of this potential difference depends on the

direction (oxidation or reduction) in which the electrode reaction proceeds. In order to express them in a uniform way, we adopt the convention that half-cell potentials are always defined for the *reduction* direction. Thus the half-cell potential for the Zn/Zn^{2+} electrode (or *couple* as it is sometimes called) is defined as the potential difference between a piece of metallic zinc and the solution when the reaction



takes place.

In the cell $\text{Zn}(s) | \text{Zn}^{2+}(aq) || \text{Cu}^{2+}(aq) | \text{Cu}(s)$ the zinc appears on the left side, indicating that it is being oxidized, not reduced. For this reason, the potential difference contributed by the left half-cell has the opposite sign to its conventional half-cell potential. More generally, we can define the *cell potential* or *cell EMF* as

$$E_{\text{cell}} = V = E_{\text{right}} - E_{\text{left}} \quad (8)$$

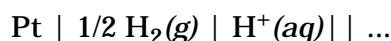
in which “right” and “left” refer to the cell notation convention (“reduction on the right”) and not, of course, to the physical orientation of a real cell in the laboratory. If we expand the above expression we see that the cell potential

$$E_{\text{cell}} = V_{\text{Cu}} - V_{\text{soln}} + V_{\text{soln}} - V_{\text{Zn}} \quad (9)$$

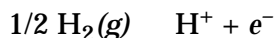
is just the *difference* between the two half-cell potentials E_{right} and E_{left} .

Reference half-cells The fact that individual half-cell potentials are not directly measurable does not prevent us from defining and working with them. Although 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 measuring the half-cell potentials on a scale that is relative to the potential of the reference cell.

The reference cell we use for this purpose is the hydrogen half-cell



in which hydrogen gas is allowed to bubble over a platinum electrode having a specially treated surface which catalyzes the reaction

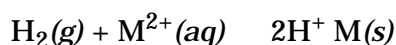


When this electrode is operated under standard conditions of 1 atm H_2 pressure, 25°C , and $\text{pH} = 0$, it becomes the **standard hydrogen electrode**, sometimes abbreviated SHE.

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



whose net reaction is



In analogy with Eq. 9, the potential difference between the platinum and M electrodes will be

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

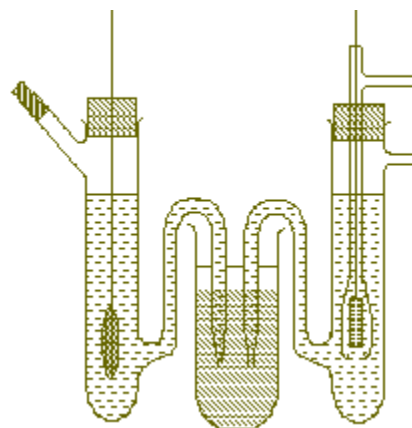


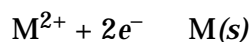
Fig. 5: Measurement of standard potentials

The hydrogen reference electrode is shown on the right, and the electrode system being measured is on the left. The two half-cells are joined by a salt bridge.

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 (relative to that of the SHE) of the half-cell whose reaction is



Standard [reduction] potentials for hundreds of electrodes have been determined (mostly in the period 1925-45, during which time they were referred to as “oxidation potentials”) and are usually tabulated in order of increasing tendency to accept electrons. This ordering is also known as the “electromotive series of the elements.” As can be seen in the abbreviated version in Table 1, sodium is the most “active” of the metallic elements in the sense that its oxidation product Na^{+} shows the smallest tendency (as indicated by the highly negative voltage) to undergo reduction.

Table 1: some standard reduction potentials

These couples (an oxidant and its conjugate reductant) are arranged in order of increasing tendency of the species in the leftmost column (oxidizing agents) to accept electrons. Each of the metals (center column) is able to donate electrons to (reduce) any oxidant below it.

The elements that appear above H_2 are called *active metals* because they are able to react with acids, reducing H^{+} to H_2 .

Notice that chlorine gas is able to remove electrons from (oxidize) water.

oxidant (electron acceptor)	reductant (electron donor)	volts
Na^{+}	$\text{Na}(s)$	-2.71 v
Zn^{2+}	$\text{Zn}(s)$	-.76
Fe^{2+}	$\text{Fe}(s)$	-.44
Cd^{2+}	$\text{Cd}(s)$	-.40
Pb^{2+}	$\text{Pb}(s)$	-.126
2H^{+}	$\text{H}_2(g)$	0.000
$\text{AgCl}(s)$	$\text{Ag}(s) + \text{Cl}^{-}(aq)$	+222
$\text{Hg}_2\text{Cl}_2(s)$	$2 \text{Cl}^{-}(aq) + \text{Hg}(l)$	+268
Cu^{2+}	$\text{Cu}(s)$	+337
$\text{I}_2(s)$	2I^{-}	+535
Fe^{3+}	Fe^{2+}	+771
Ag^{+}	$\text{Ag}(s)$	+799
$\text{O}_2(g) + 4 \text{H}^{+}$	$2 \text{H}_2\text{O}(l)$	+1.23
$\text{Cl}_2(g)$	2Cl^{-}	+1.36

2.5 Reference electrodes

In most electrochemical experiments our interest 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 are that it be easy to prepare and maintain, and that its potential be 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.

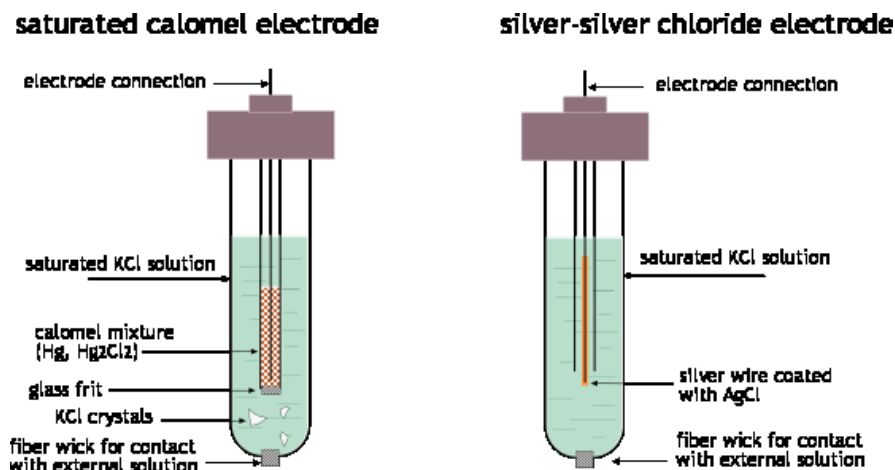


Fig. 6: Reference electrodes: the silver-silver chloride and calomel electrodes

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



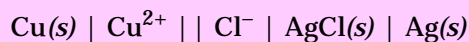
The potentials of both of these electrodes have been very accurately determined against the hydrogen electrode. The latter is seldom used in routine electrochemical measurements because it is more difficult to prepare; the platinum surface has to be specially treated by preliminary electrolysis. Also,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

3 • Prediction and significance of cell potentials

Given the 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 oxidation reaction.

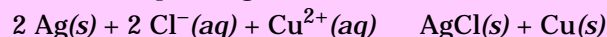
Problem Example 2:

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, the reaction will proceed to the right; 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 E° for the Cu^{2+}/Cu couple by two. The reason for this will be explained later.

3.1 Cell potentials and the electromotive series

Tables containing the same sequence of reactions as in Table 1, but without the voltage data, 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 these species 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 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 to accept electrons is relatively small. Copper, on the other hand, is a poorer electron donor, and thus its oxidized form, Cu, 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 half-cell potentials listed in Table 1 enable 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.

3.2 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, expresses the tendency for any kind of process to occur under the conditions of constant temperature and pressure. Thus and measure the same thing, and are related in a simple way:

$$G^\circ = -nFE^\circ \quad (10)$$

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 V . The right side of Eq. 10 refers to the movement of n moles of charge across the cell potential E° , and thus has the dimensions of work.
- The value of G° expresses the *maximum useful work* that a system can do on the surroundings. "Useful" work is that which can be extracted from the cell by electrical means to operate a lamp or some other external device. This excludes any P - V work that is simply a consequence of volume change (which could of course conceivably be put to some use!) and which would be performed in any case, even if the reactants were combined directly. This quantity of work – G° 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 F is expressed in coulombs per mole, the electrical work 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 1 (page 11), E° for the cell $\text{Cu}(s) \mid \text{Cu}^{2+} \parallel \text{Cl}^- \mid \text{AgCl}(s) \mid \text{Ag}(s)$ is 1.10 v; 90% of this is 1.0 v. Substituting into Eq. 10 with $n = 2$ (two electrons are transferred per mole of reaction), we have

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

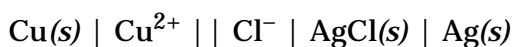
which is also the free energy change under these conditions. The cell can deliver 100 watts for $(212000/100) = 2120$ sec, or for about 35 minutes.

If Eq. 10 is solved for E° , we have

$$E^\circ = -\frac{G^\circ}{nF}$$

This states explicitly that the *cell potential is a measure of the free energy change per mole of electrons transferred*; 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.

To see this more clearly, consider the cell



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

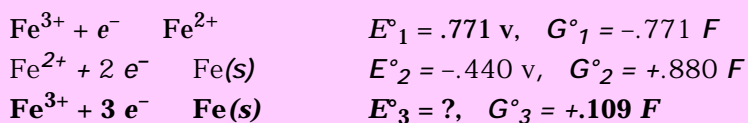
reaction	E°	$-nFE^\circ = G^\circ$
$\text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^-$ $\text{Cu}(s) \rightarrow \text{Cu}^{2+} + 2 e^-$	+ .222 v (+ .337) v	42800 J +65000 J
$2 \text{Ag}(s) + 2 \text{Cl}^-(aq) + \text{Cu}^{2+}(aq) \rightarrow 2 \text{AgCl}(s) + \text{Cu}(s)$	- .115 v	+22200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

Note, however, that if we are combining two half reactions to obtain a third half reaction, the values are not additive, since we are not eliminating electrons. Free energies are always additive, so we combine them, and use Eq. 10 to find the cell potential.

Problem Example 4:

Calculate E° for the electrode $\text{Fe}^{3+}/\text{Fe}^{2+}$ from the standard potential of the couples $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Fe^{2+}/Fe as given in Table 1 (page 11).

Solution. Tabulate the values and calculate the G° 's as follows:



The free energy for the net half-reaction is $.109nF$, 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 1 (page 11) 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 $G^\circ = RT \ln K_a$, 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 the H^+/H_2 couple, the latter level can also be regarded as the zero free energy level of the electron.

Fig. 7 shows a number of redox couples on an electron free-energy scale. Several conclusions of wide practical importance can be drawn from this table.

- For example, 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^-

Fig. 7: Electron free energy diagram for aqueous solution

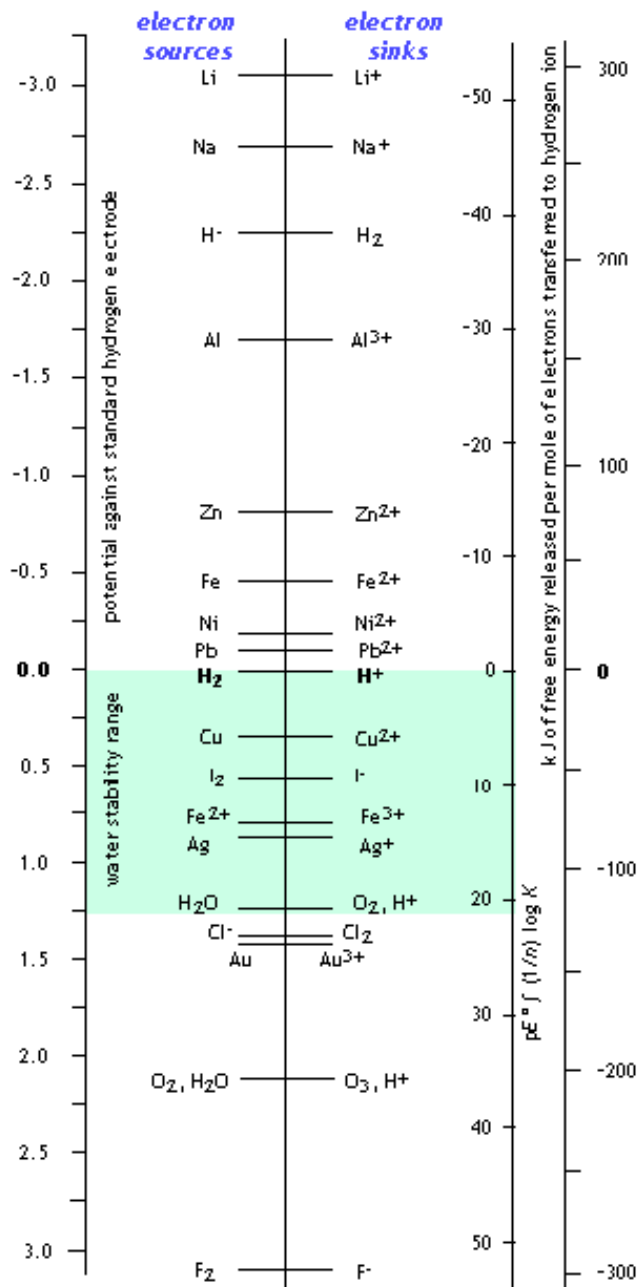
This diagram contains the same information as a table of standard potentials, but its different arrangement can provide more insight into the meaning of E° values.

The vertical axis indicates the free energies of electron when attached to various species, relative to that of the electron in H_2 . The scale on the left expresses the E° values; *i.e.* as free energies per electron-mole. The scale on the right shows the same thing in terms of kJ.

The chemical species shown on the left are oxidants (oxidizing agents) which can be regarded as possessing vacant electron-free energy levels. A redox reaction will be spontaneous only if the reductant ("electron source" in the table) is located above that of the desired "electron sink".

The similarity between this table and a table of proton free energies is striking; just as the pH defines the average proton free energy in a solution and thus controls the ratio of conjugate acid and base, 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, so if several different bases (proton sinks) are available in the same solution, they get filled from the bottom up. Redox reactions, in contrast, can be extremely slow. This means that an energetically-allowed electron transfer may not occur at an observable rate, and the outcome of an electron transfer when several oxidants are present in the same solution will be decided by kinetics rather than by thermodynamics. This explains why Cl_2 , for example does not ordinarily reduce (*i.e.*, decompose) H_2O , or why Pb is relatively inert to acids.



are both present, one would expect a higher reductant to preferentially reduce Fe^{3+} , as long the two reductions 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 decompose into hypochlorous acid (HOCl) with the evolution of oxygen. (Note, however, that this reaction is extremely slow in the absence of light.)

- Only those substances that appear between the two reactions involving water will be stable in aqueous solution in both their oxidized and reduced forms. 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, although often at a very small rate.

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 the Latimer diagram.

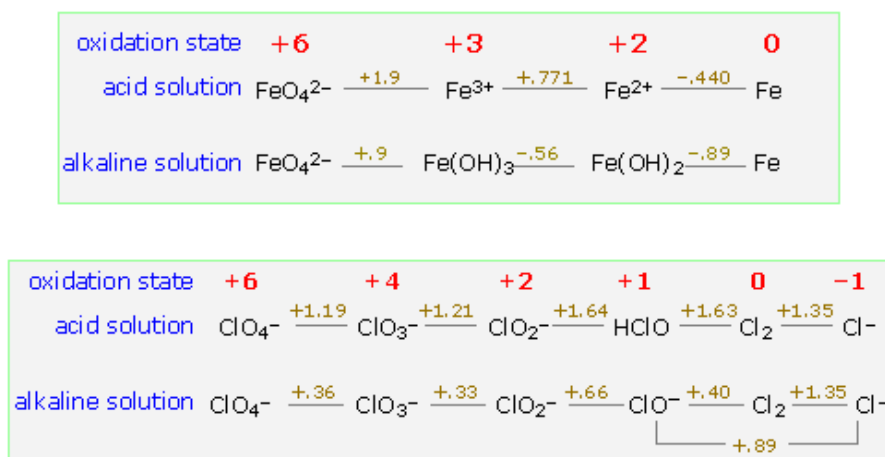
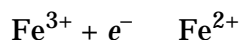


Fig. 8: Latimer diagrams

The formulas of the species that represent each oxidation state of the element are written from left to right in order of decreasing oxidation number, and the standard potential for the reduction of each species to the next on the right is written in between the formulas. Potentials for reactions involving hydrogen ions will be pH dependent (page 20), so separate diagrams are usually provided for acidic and alkaline solutions (effective hydrogen ion concentrations of 1M and 10^{-14} M, respectively).

The more positive the reduction potential, the greater will be the tendency of the species on the left to be reduced to the one on the right. To see how Latimer diagrams are used, look first at the one for iron in acid solution. The line connecting Fe^{3+} and Fe^{2+} represents the reaction



whose positive E° (.440 v) indicates that metallic iron will dissolve in acidic solution to form Fe^{2+} . Because the oxidation of this species to the +3 state has a negative potential (-.771v; moving to the left on the diagram reverses the sign), the +2 state will be the stable oxidation state of iron under these conditions.

Disproportionation An important condition to recognize is when the potential on the left of a species is less positive than that on the right. This indicates that the species can oxidize and reduce *itself*, a process known as *disproportionation*. As an example, consider Cl_2 in alkaline solution. The potential for its reduction to Cl^- is sufficiently positive (+1.35 v) to supply the

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

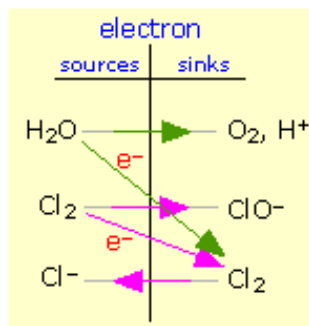
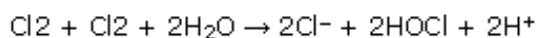


Fig. 9: Behavior of chlorine in water

Cl_2 can oxidize water (top) and also undergo disproportionation (bottom). In the latter process, one Cl_2 molecule donates electrons to another.



Bear in mind 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 two reactions shown in the figure are normally very slow.

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 1M. 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 standard effective value of 1M to an 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 G more negative than G° , 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. We begin with Eq. 10 (page 14) which relates the standard free energy change (for the complete conversion of products into reactants) to the standard potential

$$G^\circ = -nFE^\circ$$

By analogy we can write the more general equation

$$G = -nFE$$

which expresses the change in free energy for any extent of reaction— that is, for any value of the reaction quotient Q . We now substitute these into the expression that relates G and G° which you will recall from the chapter on chemical equilibrium:

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

which gives

$$-nFE = -nFE^\circ + RT \ln Q$$

which can be rearranged to

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

This is the very important *Nernst equation* which relates the cell potential to the standard potential 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:

$$E = E^\circ - \frac{0.059}{n} \log Q \quad (12)$$

Significance of the Nernst equation

This relation tells us 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 millivolts per decade concentration change. Thus for the dissolution of metallic copper



the potential

$$E = 0.337 - .0295 \log [\text{Cu}^{2+}]$$

becomes more positive (the reaction has a greater tendency to take place) as the cupric ion concentration decreases. This, of course, is exactly what the Le Châtelier Principle predicts; the more dilute the product, the greater the extent of the reaction.

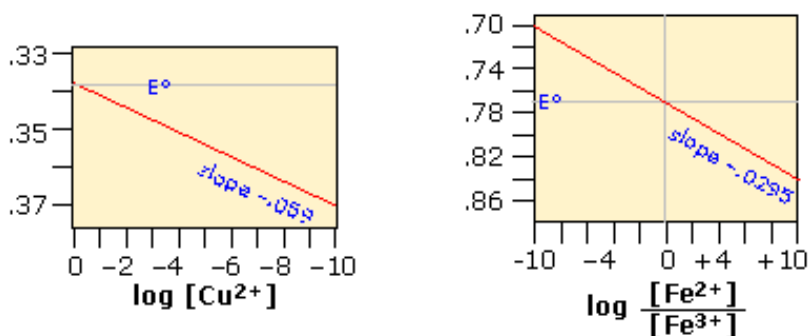


Fig. 10: Plots of the Nernst Equation

Electrodes with poise

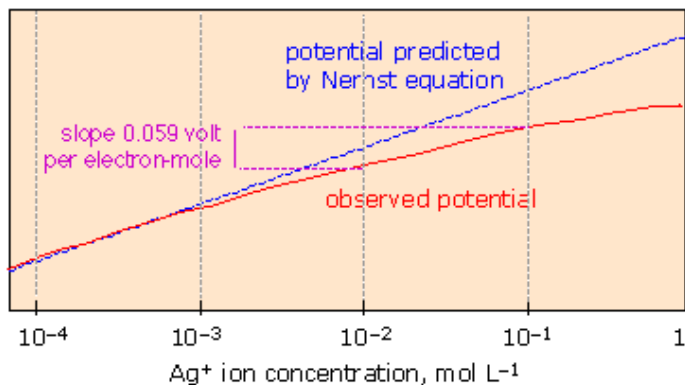
This raises an interesting question: suppose you immerse a piece of copper in a solution of pure water. With $Q = [\text{Cu}^{2+}] = 0$, the potential difference between the electrode and the solution should be infinite! Are you in danger of being electrocuted? You need not worry; without any electron transfer, there is no charge to zap you with. Of course it won't be very long before some Cu^{2+} ions appear in the solution, and if there are only a few such ions per liter, the potential reduces to only about 20 volts. More to the point, however, the system is so far from equilibrium (for example, there are not enough ions to populate the electric double layer) that the Nernst equation doesn't really give meaningful results. Such an electrode is said to be *unpoised*. What ionic concentration is needed to poise an electrode? I don't really know, but I would be suspicious of anything much below $10^{-6} M$.

The Nernst equation works only in *dilute* ionic solutions

Ions of opposite charge tend to associate into loosely-bound *ion pairs* in more concentrated solutions, thus reducing the number of ions that are free to donate or accept electrons at an electrode. For this reason, the Nernst equation cannot accurately predict half-cell potentials for solutions in which the total ionic concentration exceeds about 10^{-3} M.

Fig. 11: Concentration-dependence of half-cell potential

The Nernst Equation accurately predicts half-cell potentials only when the equilibrium quotient term Q is expressed in activities. Ionic activities depart increasingly from concentrations when the latter exceed 10^{-4} - 10^{-3} M, depending on the size and charge of the ion.



Activities and activity coefficients

If the Nernst equation is applied to more concentrated solutions, the terms in the reaction quotient Q must be expressed in “effective concentrations” or **activities** of the electroactive ionic species. The **activity coefficient** (γ) relates the concentration of an ion to its activity a in a given solution through the relation $a = \gamma c$. Since electrode potentials 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 E_s can then be used to convert concentrations into activities for use in other calculations involving equilibrium constants.

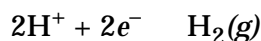
Cell potentials and pH; stability diagrams

As most of us recall from our struggles with balancing redox equations in our beginning chemistry courses, many electron-transfer reactions involve hydrogen ions and hydroxide ions. The standard potentials for these reactions therefore refer to the pH, either 0 or 14, at which the appropriate ion has unit activity. Because multiple numbers of H^+ or OH^- ions are often involved, the potentials given by the Nernst equation can vary greatly with the pH.

It is frequently useful to look at the situation in another way by considering what combinations of potential and pH allow the stable existence of a particular species. This information is most usefully expressed by means of a E -vs.- pH diagram, also known as a *Pourbaix* diagram.

Stability of water

As was noted in connection with the shaded region in Fig. 7 (page 16), water is subject to decomposition by strong oxidizing agents such as Cl_2 and by reducing agents stronger than H_2 . The reduction reaction can be written either as



or, in neutral or alkaline solutions as



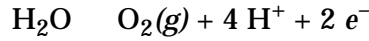
These two reactions are equivalent and follow the same Nernst equation

$$E_{H^+/H_2} = E^0_{H^+/H_2} + \frac{RT}{nF} \ln \frac{[H^+]^2}{P_{H_2}}$$

which, at 25°C and unit H₂ partial pressure reduces to

$$E = E^0 - 0.059 \text{ pH} = -0.059 \text{ pH} \tag{13}$$

Similarly, the oxidation of water



is governed by the Nernst equation

$$E_{O_2/H_2O} = E^0_{O_2/H_2O} + \frac{RT}{nF} \ln P_{O_2} \cdot [H^+]^4$$

which can also be represented by Eq. 13. From this information we can construct the stability diagram for water shown below.

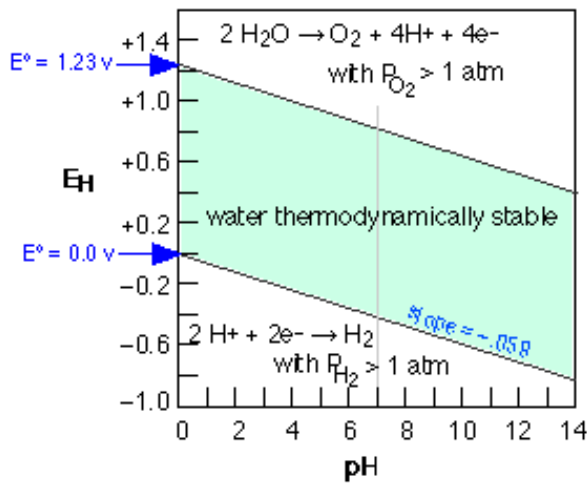


Fig. 12: Stability (Pourbaix) diagram for water

This diagram has special relevance to electrochemical corrosion (see page 32.) Thus metals above H₂ in activity series will tend to undergo oxidation (corrosion) by reducing H⁺ ions or water. The unity partial pressures are of course purely arbitrary criteria; in a system open to the atmosphere, water can decompose even at much lower hydrogen partial pressures.

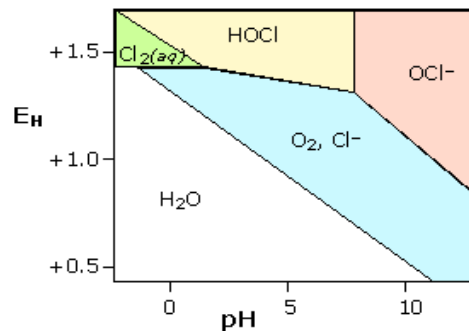
Chlorine in water

Because chlorine is widely used as a disinfectant for drinking water, swimming pools, and sewage treatment, it is worth looking at its stability diagram. Note that the effective bactericidal agent is not Cl_2 itself, but its oxidation product hypochlorous acid HOCl which predominates at pH values below its pK_a of 7.3. Note also that

- Cl_2 is unstable except at very low pH; it decomposes into HOCl and Cl^- .
- Hypochlorous acid and its anion are stronger oxidants than O_2 and thus subject to decomposition in water. The only stable chlorine species in water is Cl^- .
- Decomposition of HOCl occurs very slowly in the dark, but is catalyzed by sunlight. For this reason the chlorine in outside swimming pools must be frequently renewed.
- Decomposition of Cl_2 and HOCl by reaction with organic material in municipal water supply systems sometimes makes it necessary to inject additional chlorine at outlying locations.

Fig. 13: Stability diagram for chlorine in water

Equilibria between species separated by diagonal lines are dependent on both E and pH, while those separated by horizontal or vertical lines are affected by pH only or E only, respectively.



Iron

Stability diagrams are able to condense a great amount of information into a compact representation, and are widely employed in geochemistry and corrosion engineering. The Pourbaix diagram for iron is one of the more commonly seen examples.

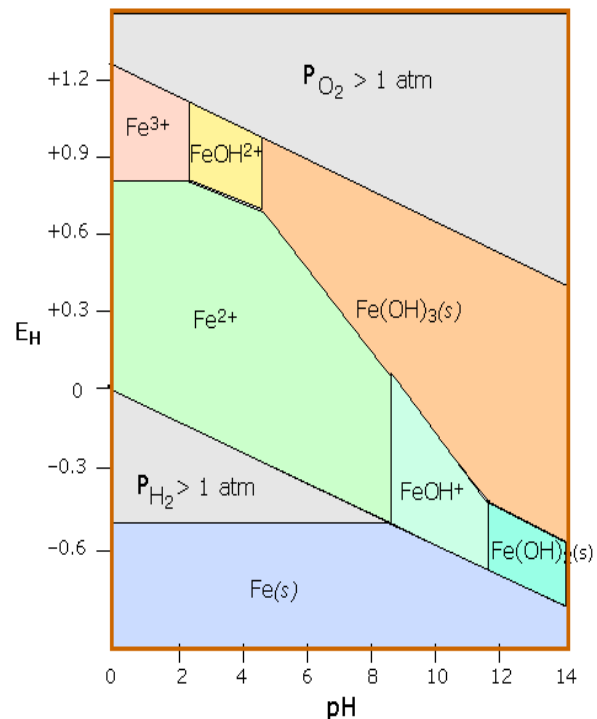
Fig. 14: Pourbaix diagram for iron

Three oxidation states of iron (0, +2 and +3) are represented on this diagram. The stability regions for the oxidized iron states are shown only within the stability region of H_2O . Equilibria between species separated by vertical lines are dependent on pH only.

The +3 oxidation state is the only stable one in environments in which the oxidation level is controlled by atmospheric O_2 . This is the reason the Earth's crust contains iron oxides, which developed only after the appearance of green plants which are the source of O_2 .

Iron is attacked by H^+ to form H_2 and Fe(II) ; the latter then reacts with O_2 to form the various colored Fe(III) oxides that constitute "rust".

Numerous other species such as oxides and hydrous oxides are not shown. A really "complete" diagram for iron would need to have at least two additional dimensions showing the partial pressures of O_2 and CO_2 .



4.1 Concentration cells

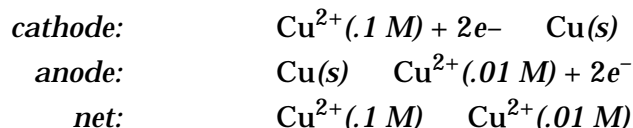
From your study of thermodynamics you may recall that the process



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 driving force for this process is the free energy change G associated with the concentration gradient ($C_2 - C_1$), sometimes known as the *free energy of dilution*:

$$G_{\text{dilution}} = RT \ln(C_2/C_1)$$

Note, however, that Cu^{2+} ions need not physically move between the two compartments; electron flow through the external circuit creates a “virtual” flow as copper ions are created in the low-concentration side and discharged at the opposite electrode. Nitrate ions must also pass between the cells to maintain electroneutrality.

The Nernst equation for this cell is

$$E = E^\circ - (0.059/\text{N}) \log Q = 0 - 0.29 \log 0.1 = +0.285 \text{ v}$$

Note that E° for a *concentration cell* is always zero, since this would be the potential of a cell in which the electroactive species are at unit activity in both compartments.

4.2 Thermodynamics of galvanic cells

The free energy change for a process represents the maximum amount of non-*PV* work that can be extracted from it. In the case of an electrochemical cell, this work is due to the flow of electrons through the potential difference between the two electrodes. Note, however, that as the rate of electron flow (i.e., the current) increases, the potential difference must decrease; if we short-circuit the cell by connecting the two electrodes with a conductor having negligible resistance, the potential difference is zero and no work will be done. The full amount of work can be realized only if the cell operates at an infinitesimal rate- that is, *reversibly*.

The total amount of energy a reaction can supply under standard conditions at constant pressure and temperature is given by H° . If the reaction takes place by combining the reactants directly (no cell) or in a short-circuited cell, no work is done and the heat released is

H . If the reaction takes place in a cell that performs electrical work, then the heat released is diminished by the amount of electrical work done. In the limit of reversible operation, the heat released becomes

$$H = G^\circ + T \Delta S$$

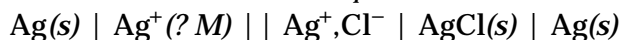
4.3 Analytical applications of the Nernst equation

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

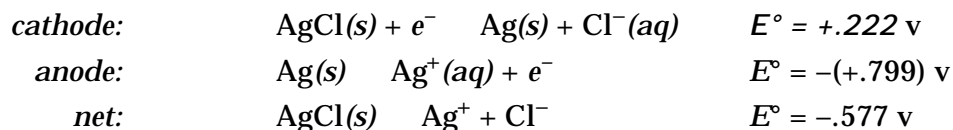
using relatively simple physical techniques is bound to be widely exploited. Cell potentials are fairly easy to measure, and although the Nernst equation relates them to ionic activities rather than to concentrations, the difference between them becomes negligible in solutions where the total ionic concentration 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 cell



whose net equation corresponds to the dissolution of silver chloride:



The standard potential for the net reaction refers to a hypothetical solution in which the activities of the two ions are unity. The cell potential we actually observe corresponds to E in the Nernst equation, which is then solved for Q which gives K_{sp} directly.

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 is added, the ferrous ion is oxidized to Fe^{3+} in a reaction that is virtually complete:

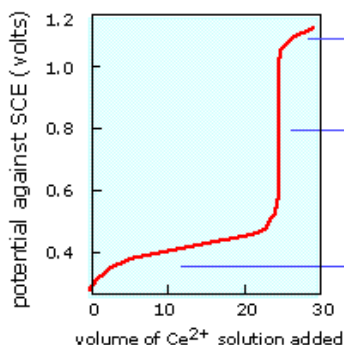


The cell potential is followed as the Fe^{2+} is added in small increments. Once the first drop of titrant has been added, the potential of the left cell is controlled by the ratio of oxidized and reduced iron according to the Nernst equation

$$E = 0.68 - 0.059 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

Fig. 15: Potentiometric titration

Plot showing how the cell potential changes when FeSO_4 is titrated with $\text{Ce}(\text{SO}_4)_2$. Note that the potential is controlled by different reactions on either side of the equivalence point.



Beyond the end point there is no more Fe^{2+} , so the potential rises rapidly to that of a $\text{Ce}^{4+}/\text{Ce}^{3+}$ cell with excess Ce^{4+} .

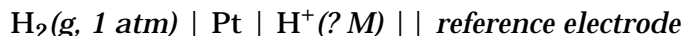
Equivalence point at steepest part of plot

Initially, the solution is mostly Fe^{2+} . As Ce^{4+} is added, the iron is oxidized and the potential slowly rises as the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio decreases.

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 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 $\{\text{H}^+\}$ and thus of $-\log \{\text{H}^+\}$, which is the pH.



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.

The glass electrode for pH measurements

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 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.

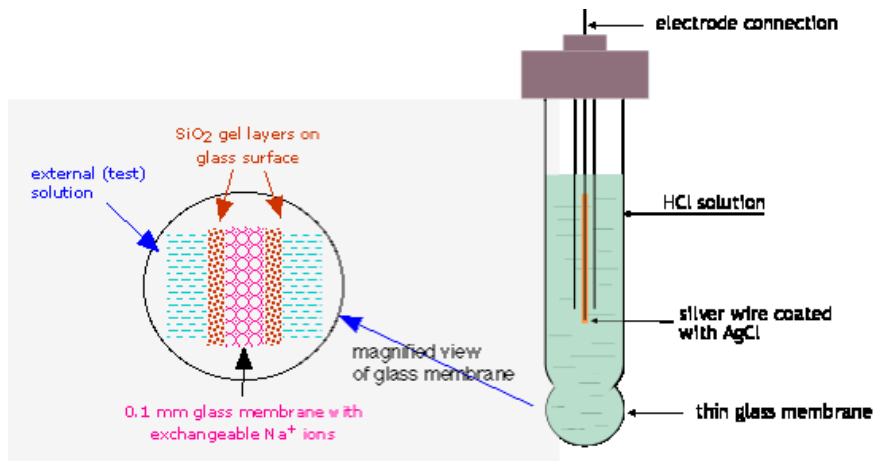


Fig. 16: The glass electrode for pH measurements

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 H₂:

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

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 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

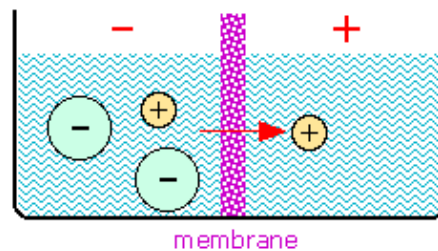
The function of the membrane in the glass electrode is to allow hydrogen ions to pass through and thus change its potential, while preventing other cations from doing the same thing (this selectivity is never perfect; most glass electrodes will respond to moderate concentrations of sodium ions, and to high concentrations of some others.) 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.

4.4 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. 17: Origin of a membrane potential

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



The figure 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 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:

$$= \frac{RT}{nF} \ln \frac{\{K^+\}_{right}}{\{K^+\}_{left}} = \frac{RT}{nF} \ln \frac{\{Cl^-\}_{left}}{\{Cl^-\}_{right}}$$

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, the above equation predicts that the potential difference $_{inside} - _{outside}$ will be

$$= 0.059 \log \frac{1}{20} = -70 \text{ mv}$$

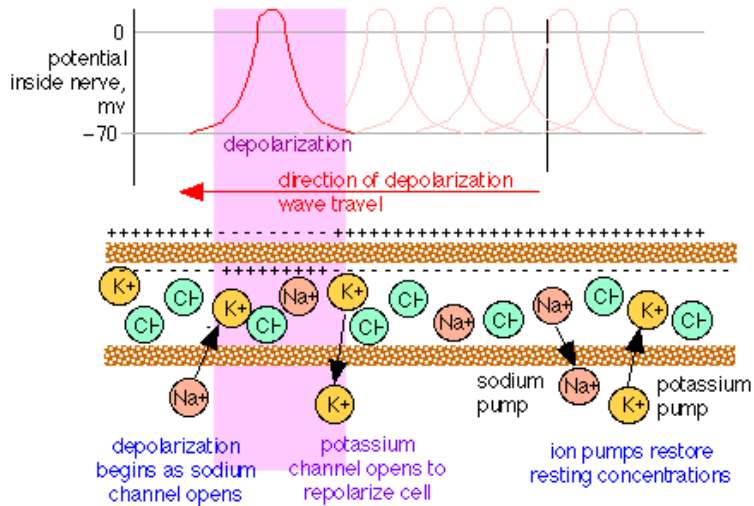
which is consistent with observed values. Transport of an ion such as K^+ from a region of low concentration into the more concentrated intercellular fluid requires a source of free energy, which is supplied by ATP under enzymatic control. The metabolic processes governing this action are often referred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

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 differential ion concentrations that travel along the length of the nerve. These concentration gradients are reduced by protein-based *ion channels* and ATP-activated (and energy-consuming) *ion pumps* specific to K^+ and Ca^{2+} ions.

Fig. 18: Conduction of nerve impulses

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

One of the oldest and most important applications of electrochemistry is to the storage and conversion of energy. You already know that a *galvanic cell* converts chemical energy to work; similarly, an *electrolytic cell* converts electrical work into chemical *free energy*. Devices that carry out these conversions are called **batteries**. In ordinary batteries the chemical components are contained within the device itself. If the reactants are supplied from an external source as they are consumed, the device is called a **fuel cell**.

The term *battery* derives from the older use of this word to describe physical attack or "beating"; Benjamin Franklin first applied the term to the electrical shocks that could be produced by an array of charged glass plates. In common usage, the term "cell" is often used in place of battery.

5.1 The ideal and the real

For portable and transportation applications especially, a battery or fuel cell should store (and be able to deliver) the maximum amount of energy at the desired rate (power level) from a device that has the smallest possible weight and volume. The following parameters are commonly used to express these attributes:

- Storage capacity or *charge density*, coulombs/liter or coulombs/kg;
- *Energy density*, J/kg or watt-hour/lb
- *Power density*, watts/kg
- *Voltage efficiency*, ratio of output voltage to E°
- Lifetime: *shelf-life* (resistance to self-discharge) or *charge/recharge cycles*

Physical limitations of battery performance

The most important of these are:

- *Effective surface area of the electrode*. A 1-cm^2 sheet of polished metal presents far less active surface than does one that contains numerous surface projections or pores. All useful batteries and fuel cells employ highly porous electrodes.

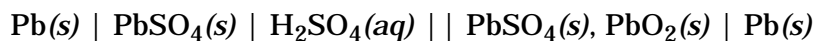
- *Current density of electrode surface.* Expressed in amperes m^{-2} , this is essentially a measure of the catalytic ability of the electrode, that is, its ability to reduce the activation energy of the electron transfer process.
- *Rate at which electroactive components can be delivered to or depart from the active electrode surface.* These processes are controlled by thermal diffusion and are inhibited by the very narrow pores that are needed to produce the large active surface area.
- *Side reactions and irreversible processes.* The products of the discharge reaction may tend to react with the charge-storing components. Thermal diffusion can also cause self-discharge, limiting the shelf life of the battery. Recharging of some storage batteries may lead to formation of less active modifications of solid phases, thus reducing the number of charge/discharge cycles possible.

Clearly, these are all primarily kinetic and mechanistic factors which require a great deal of experimentation to understand and optimize.

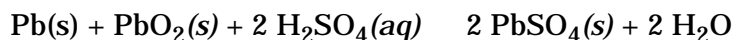
5.2 Primary and secondary batteries

The electrode reactions in a *secondary* or *storage* battery can proceed in either direction, so the battery is capable of being recharged. During charging, electrical work is done on the cell to provide the free energy needed to force the reaction in its 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 GASTON PLANTÉ in 1859 and is still the most widely used device of its type. The cell is represented by

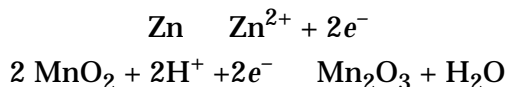


and the net cell reaction is



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 most well-known primary battery has long been the common “dry cell” that is widely used to power flashlights and similar devices. The modern dry cell is based on the one invented by GEORGES LECLANCHE in 1866. The electrode reactions are



Despite its name, this cell is not really “dry”; the electrolyte is a wet paste containing NH_4Cl to supply the hydrogen ions. The chemistry of this cell is more complicated than it would appear from these equations, and there are many side reactions. A more modern version, introduced in 1949, is the *alkaline cell* which employs a KOH electrolyte and a zinc-powder anode which permits the cell to deliver higher currents.

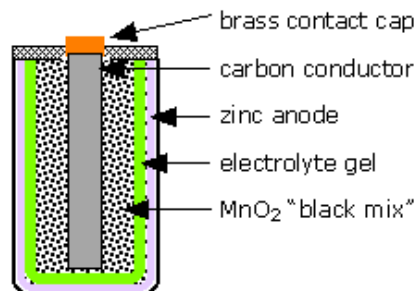


Fig. 19: A modern Leclanche cell

5.3 Timeline of battery development

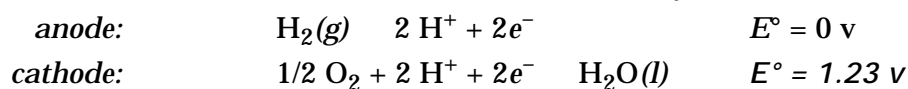
“Baghdad Battery”	Earthenware jars containing an iron rod surrounded by a copper cylinder were discovered near Baghdad in 1938. They are believed to have been used by the Parthian civilization that occupied the region about 2000 years ago as a source of electricity to plate gold onto silver.
Allesandro Volta 1782	His "Voltaic pile", a stack of zinc and silver disks separated by a wet cloth containing a salt or a weak acid solution, was the first battery known to Western civilization.
Sir Humphry Davy 1813	Davy builds a 2000-plate battery that occupies 889 square feet in the basement of Britain's Royal Society
Michael Faraday, 1830's	Faraday discovered the fundamentals of galvanic cells and electrolysis that put electrochemistry on a firm scientific basis.
1836 – Daniell cell (also known as a Crow's Foot or Gravity cell.)	John Daniell (English physicist) developed the first modern storage cell based on Faraday's principles. This consists of a large glass jar with a copper star-shaped electrode in the bottom and a zinc "crow's foot" shaped electrode suspended near the top. The bottom of the jar was filled with a concentrated copper sulfate solution. On top of this was poured dilute sulfuric acid, whose lower density kept it on top. This was the first practical battery to find wide use to power telegraphs and railway signaling systems and home door-bells.
1839 – William Grove (English)	Grove discovered "reverse electrolysis" following electrolysis of water at platinum electrodes; proposed the hydrogen-oxygen fuel cell.
1859 – Gaston Planté (French)	Invents the first practical lead-acid storage cell
1866 – Georges Leclanche (French)	By 1868 twenty thousand Leclanche cells were being used in telegraph systems. The original Leclanche cells were built in porous pots which were heavy and subject to breakage. Within twenty years other inventors had modified the design into what we now know as "dry cells" which became widely used in the first flashlights (1909) and in battery-powered radios of the 1920s.
1905 Nickel-iron cell (Thomas Edison)	Edison, who was as much a chemist as an all-around inventor, thought that the lead in Planté-type cells made them too heavy, and that having acid in contact with any metal was an inherently bad idea. The Edison cell uses an iron anode, nickel oxide cathode, and KOH electrolyte. This cell is extremely rugged and is still used in certain industrial applications, but it was never able to displace the lead-acid cell as Edison had hoped..
1950s	A similar cell, employing a nickel anode instead of iron, was the first rechargeable cell that was small enough to be used in portable consumer devices. Its main disadvantage is that it is ruined by complete discharge.
1949 – Urry (Eveready Battery Co.)	First commercial alkaline dry cell.

Mercury cell (Ruben and Mallory, 1950's)	This was one of the first "button"-type cells which were widely used in cameras and hearing aids. Most countries have outlawed the sales in order to reduce mercury contamination of the environment.
1959 - Fuel cell (Bacon)	The first practical fuel cell developed by British engineer Francis Bacon. This H ₂ -O ₂ cell used an alkaline electrolyte and inexpensive nickel electrodes.
Nickel-Cadmium (NiCad) cells	quickly become one of the most popular rechargeable batteries for small consumer devices. They can deliver high current and undergo hundreds of charge-discharge cycles. Because cadmium is an environmental toxin, their use is being discouraged.
Late 1960's – Nickel-metal hydride cells.	The hydride ion H ⁻ would be an ideal cathode material except for the fact that its oxidation product H ₂ is a gas. The discovery that certain compounds such as LiNi ₅ and ZrNi ₂ can act as "hydrogen sponges" made it practical to employ metal hydrides as a cathode material. One peculiarity of Ni-MH cells is that recharging them is an exothermic process, so that proper dissipation of heat must be allowed for.
Lithium cells	Lithium is an ideal anode material owing to its low density and high reduction potential, making Li-based cells the most compact ways of storing electrical energy. Many types of Li cells have been developed; early ones used a MnO ₂ cathode and were limited to low-current applications. The latter restriction has been overcome in the most recent lithium cells which employ an iron-disulfide cathode and a solid polymeric electrolyte

5.4 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 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*.

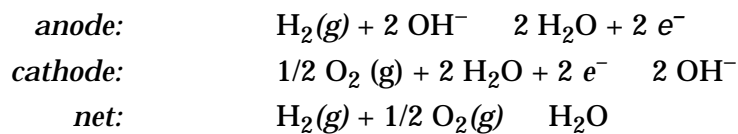
Although fuel cells were not employed for practical purposes until space exploration began in the 1960's, the principle was first demonstrated in 1839 by Sir William Grove, a lawyer and amateur chemist. At the time, it was already known that water could be decomposed into hydrogen and oxygen by electrolysis; 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:



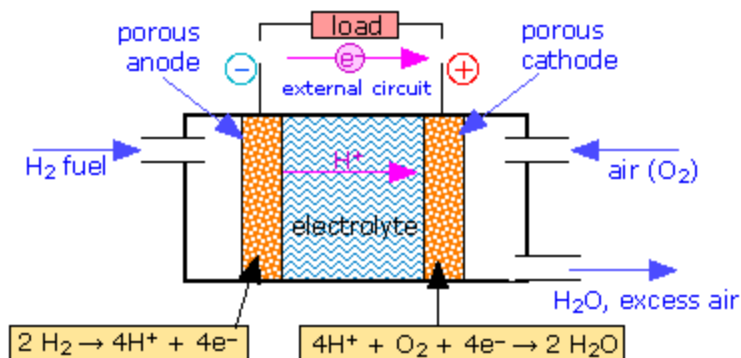
It was not until 1959 that the first working hydrogen-oxygen fuel cell was developed. Modern cells employ an alkaline electrolyte, so the electrode reactions differ from the one shown above by the addition of OH⁻ to both sides of the equations (note that the net reaction is the same):



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.

Fig. 20: Fuel cell

In a fuel cell, the oxidation and reduction steps take place in separate compartments, unlike in conventional combustion. The fuel in this particular cell is hydrogen, but methanol or any other fuel can also be used. Developing suitably active and permanent catalytic electrode surfaces is the principal engineering problem.



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 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 $-H^\circ = 242 \text{ kJ mol}^{-1}$, but no more than about half of this heat can be converted into work so the output would not exceed 121 kJ mol⁻¹.

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

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 usable 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 can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process $\text{M} \rightarrow \text{M}^+ + \text{e}^-$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a **depolarizer**.

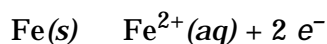
In a sense, corrosion can be viewed as the spontaneous return of metals to their ores; the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes.

The economic aspects of corrosion are far greater than most people realize; according to a report published in 2001, the cost of corrosion in the U.S. alone was \$276 billion per year. Of this, about \$121 billion was spent to control corrosion, leaving the difference of \$155 billion as the net loss to the economy. Utilities, especially drinking water and sewer systems, suffer

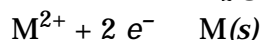
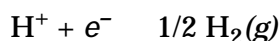
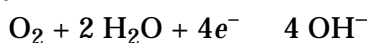
the largest economic impact with motor vehicles and transportation being a close second.

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. Oxygen, of course, is the most prominent of these, but hydrogen ions and the cations of any more "noble" metal¹ are also very common promoters of corrosion.

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

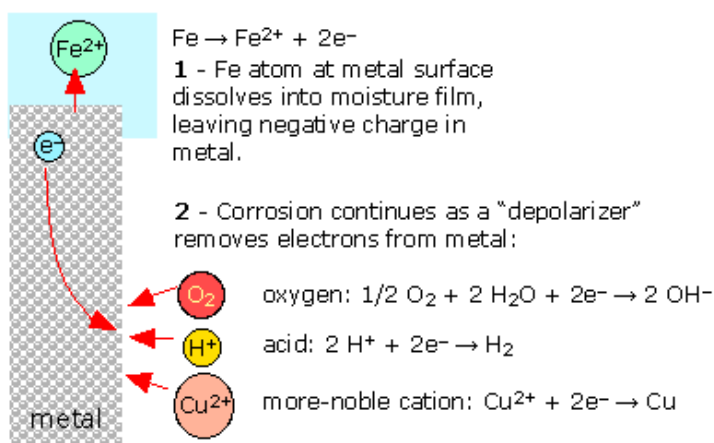


where M is a metal. A thin film of moisture on the surface of the metal can serve as the medium for the electrolyte.

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.

Fig. 21: Electrochemical corrosion of iron

Corrosion often begins at a location where the metal is stressed in some way or isolated from oxygen, such as between joints or under a paint film. The metal ions dissolve in the moisture film and the electrons migrate to another location where they are taken up by a "depolarizer". Oxygen is the most common depolarizer; the resulting hydroxide ions react with the Fe^{2+} to form the mixture of hydrous iron oxides known as "rust".



For part of a metal to act as the site for oxidation and dissolution, it must be in contact with

1. A noble metal is one that appears toward the bottom of a listing of standard reduction potentials as in Table 1 (page 11). From Fig. 7, you can see that such metals serve as lower-free energy sinks which can accept electrons from higher (less noble) metals.

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 corrosion¹.

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.

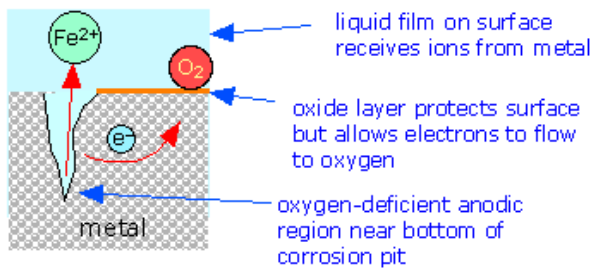


Fig. 22: Pitting corrosion

Most metals are covered with thin layer of oxide film which inhibits anodic dissolution. When corrosion does occur, it sometimes 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. Many oxides have semiconductive properties and thus do not interfere with the flow of electrons to O_2 .

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. 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.

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.

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

Control of corrosion

Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of either 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 approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction $M \rightarrow M^{2+} + 2 e^{-}$ to take place.

Sacrificial coatings One way of supplying this negative charge is to apply a coating of a more active metal. Thus a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as *galvanizing*. 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.

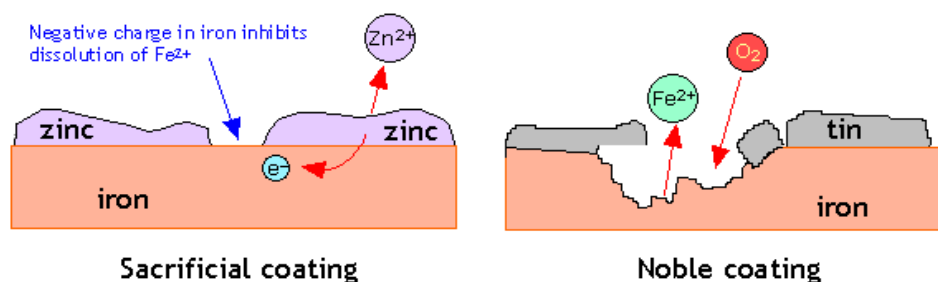


Fig. 23: Corrosion protection by sacrificial coating, and its reverse.

The effect of plating iron with a less active metal provides an interesting contrast. The common tin-plated can (on the right) 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.

Cathodic protection. Another way of keeping metal in a cathodic state is to connect it to an external direct current source. For smaller structures such as boats and domestic water heaters the current is supplied by a sacrificial anode made of aluminum or zinc. For larger extended structures such as piers and buried pipelines, an external line-operated or photovoltaic power supply is commonly used. (All interstate oil pipelines in the U.S. are required by law to employ cathodic protection.)

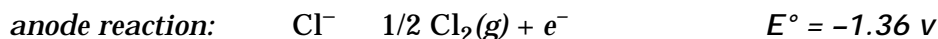
7 • Electrolytic cells

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 these two metallic elements and showed that these two hydroxides which had previously been considered un-decomposable and thus elements, were in fact compounds:

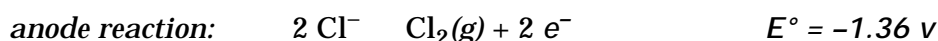
"By means of a flame which was thrown on a spoon containing potash, this alkali was kept for some minutes at a strong red heat, and in a state of perfect fluidity." One pole of a battery of copper-zinc cells was connected to the spoon, and the other was connected to plati-

num 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, Davey 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 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.

A common misconception about electrolysis is that "ions are attracted to the oppositely-charged electrode." This is true only in the very thin interfacial region near the electrode surface. Ionic motion throughout the bulk of the solution is by *diffusion*, which is the transport of molecules in response to a concentration gradient. *Migration*—the motion of a charged particle due to an applied electric field, is only a minor player, producing only about one non-random jump out of around 100,000 random ones for a 1 volt cm^{-1} electric field. Only those ion that find themselves within the interfacial region are likely to undergo migration.

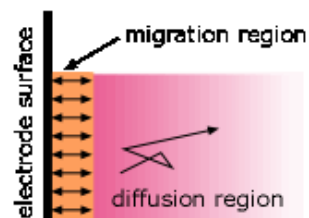
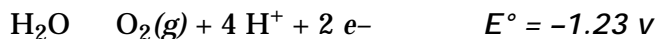


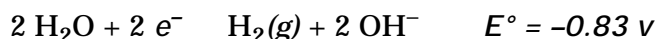
Fig. 24: Diffusion and migration in an electrolytic cell

7.1 Electrolysis in aqueous solutions

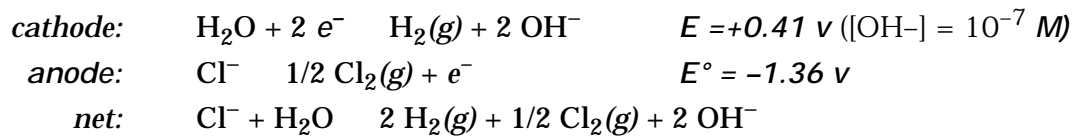
Water is capable of undergoing both *oxidation*



and *reduction*

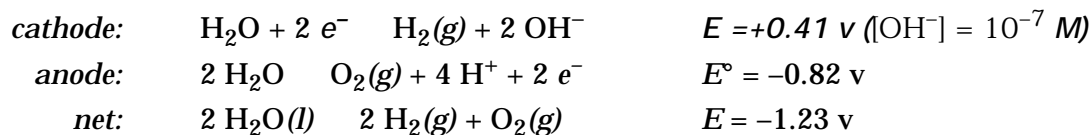


Thus if an aqueous solution is subjected to electrolysis, one or both of the above reactions may be able to compete with the electrolysis of the solute. This does not happen for the solution of NiCl_2 illustrated above, but if we substitute sodium chloride for nickel chloride, hydrogen is produced at the cathode instead of sodium:



The reason metallic sodium is not a product of this reaction is best understood by locating the couples Na/Na^+ and $\text{H}_2\text{O}/\text{H}_2$, OH^- in Fig. 7 (page 16). 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.

If we replace the chloride ion in the above reaction with an anion such as nitrate or sulfate that is energetically 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:



7.2 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.

Most stoichiometric problems involving electrolysis can be solved without explicit use of Faraday's laws. The "chemistry" in these problems is usually very elementary; the major difficulties usually stem from unfamiliarity with the basic electrical units:

- *current* (amperes) is the rate of *charge transport*; 1 amp = 1 c/sec.
- *power* (watts) is the rate of *energy* production or consumption; 1 w = 1 J/sec = 1 volt-amp; 1 watt-sec = 1 J, 1 kw-h = 3600 J.

Example 5:

An object to be plated with copper is placed in a solution of CuSO_4 .
 Which electrode of a direct current power supply should the object be connected?
 How much mass of copper will be deposited if a current of 0.22 amp flows through the cell for 24 hours?

Since Cu^{2+} ions are being reduced, the object acts as a cathode and must be connected to the negative terminal (where the electrons come from!)

The amount of charge passing through the cell is

$$(0.22 \text{ amp}) \times (86400 \text{ sec}) = 19008 \text{ c}$$

$$(19008 \text{ c}) \div (96500 \text{ c F}^{-1}) = 0.197 \text{ F}$$

The reduction of one mole of Cu^{2+} ion requires the addition of two moles of electrons, so the cell discharges only 0.0985 mol of Cu^{2+} whose mass will be

$$(0.0985 \text{ mol}) \times (63.54 \text{ g mol}^{-1}) = 6.26 \text{ g of copper}$$

Problem Example 6:

How much electric power is required to produce 1 metric ton (1000 kg) of chlorine from brine, assuming the cells operate at 2.0 volts and assuming 100 % efficiency?

Solution:

$$\text{moles of Cl}_2 \text{ produced: } (1000 \text{ kg}) \div 70 \text{ g mol}^{-1} = 14300 \text{ mol Cl}_2$$

$$\text{faradays of charge: } (2 \text{ F/mol}) \times (14300 \text{ mol}) = 28600 \text{ F}$$

$$\text{charge in coulombs: } (96500 \text{ c/F}) \times (28600 \text{ F}) = 2.76 \times 10^9 \text{ c}$$

$$\text{duration of electrolysis: } (3600 \text{ s/h}) \times (24 \text{ h}) = 86400 \text{ s}$$

$$\text{current (rate of delivery): } (2.76 \times 10^9 \text{ amp-sec}) \div (86400 \text{ sec}) = 32000 \text{ amps}$$

$$\text{power (volt-amps): } (2.0 \text{ v}) \times (32000 \text{ a}) = 64.0 \text{ kw}$$

$$\text{energy in kW-h: } (64.0 \text{ kw}) \times (24 \text{ h}) = 1536 \text{ kw-h}$$

$$\text{energy in joules: } (1536 \text{ kw-h}) \times (3.6 \text{ MJ/kw-h}) = 5530 \text{ MJ}$$

(In the last step, recall that $1 \text{ w} = 1 \text{ j/s}$, so $1 \text{ kw-h} = 3.6 \text{ MJ}$)

7.3 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^- .

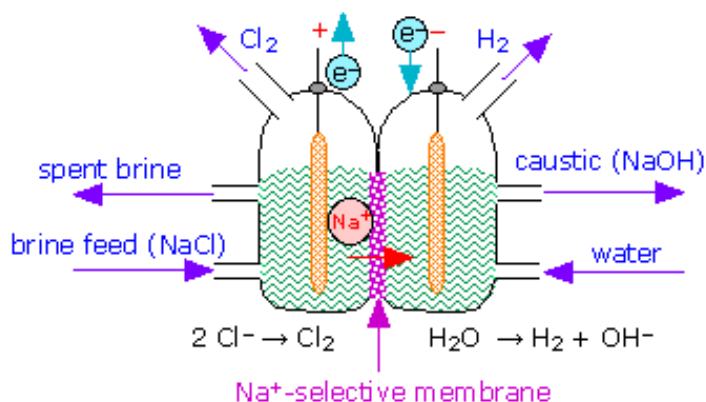
anode reactions	$2 \text{Cl}^- \rightarrow \text{Cl}_2(g) + 2 e^-$	-1.36 v	<i>i</i>
	$4 \text{OH}^- \rightarrow \text{O}_2(g) + 2 \text{H}_2\text{O} + 4 e^-$	-0.40 v	<i>ii</i>
cathode reactions	$\text{Na}^+ + e^- \rightarrow \text{Na}(s)$	-2.7 v	<i>iii</i>
	$\text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-$	+0.41 v	<i>iv</i>

A comparison of the E° s would lead us to predict that the reduction (*ii*) would be favored over that of (*i*). This is certainly the case from a purely energetic standpoint, but as was mentioned in the section on fuel cells, electrode reactions involving O_2 are notoriously slow (that is, they are *kinetically hindered*), so the anodic process here is under kinetic rather than thermodynamic control. The reduction of water (*iv*) is energetically favored over that of Na^+ (*iii*), so the net result of the electrolysis of brine is the production of Cl_2 and NaOH (“*caustic*”), both of which are of immense industrial importance:



Fig. 25: Schematic diagram of a modern cell for the production of chlorine

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 and is the most abundant metallic element in the earth's crust (eight percent by weight.) However, its isolation is very difficult and expensive to accomplish by purely chemical means, as evidenced by the high E° (-1.66 v) 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.

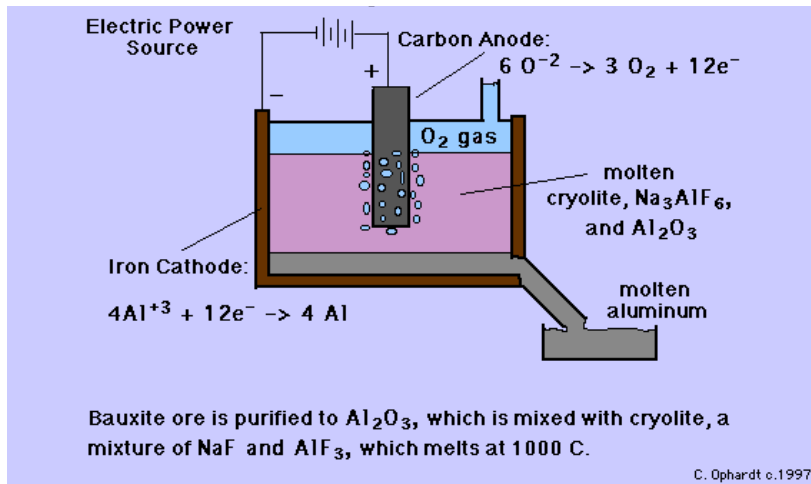


Fig. 26: Hall-Héroult cell for the production of aluminum

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.