

the fraction of HI that decomposes
show that this fraction does not de-

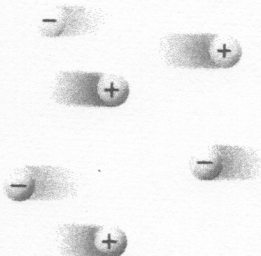
ion

late the concentration of AB in a
60 mole of B have been injected.

Ans. $3.0 \times 10^{-2} M$

PCl_5 is heated, it decomposes to
1 that the equilibrium mixture of
r liter when the pressure is 1.00
decomposition in moles per liter.

Ans. 0.073



14 Electrochemistry

WHEN A CHEMICAL REACTION OCCURS, there is a net increase or decrease in potential energy. In most cases, the change in potential energy appears as heat evolved or absorbed from the surroundings. Occasionally, however, the change in potential energy may be made to appear as electric energy. In this chapter, the relation between chemical energy and electric energy is explored. We consider the transport of electric energy through matter, the conversion of electric energy into chemical energy, and the conversion of chemical energy into electric energy. These topics belong to the field of *electrochemistry*.

14.1 ELECTRIC CONDUCTIVITY

Electric energy may be transported through matter by the conduction of electric charge from one point to another in the form of an *electric current* (see Appendix 4.5 to 4.7 for discussion of electrical terms). In order that the electric current exist, there must be charge carriers in the matter, and there must be a force that makes the carriers move. The charge carriers can be electrons, as in the case of metals, or they can be positive and nega-

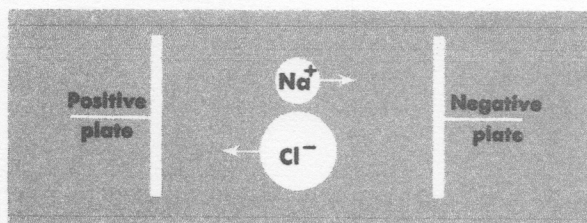


Fig. 14.1 Electric forces on ions in solution.

tive ions, as in the case of electrolytic solutions and molten salts. In the former case, conduction is said to be *metallic*; in the latter, *electrolytic*. The electric force that makes charges move is usually supplied by a battery or some similar source of electrical energy. Any region of space in which there is an electric force is called an *electric field*.

As pointed out in Sec. 8.4, solid metals consist of ordered arrays of positive ions immersed in a sea of electrons. For example, silver consists of Ag^+ ions arranged in a face-centered-cubic pattern with the entire lattice permeated by a cloud of electrons equal in number to the number of Ag^+ ions in the crystal. The Ag^+ ions are more or less fixed in positions from which they do not move except under great stress. The electrons of the cloud, on the contrary, are free to roam throughout the crystal. When an electric field is impressed on the metal, the electrons migrate and thereby carry negative electric charge through the metal. In principle, it should be possible for an electric field to force all the loose electrons toward one end of a metal sample. In practice, it is extraordinarily difficult to separate positive and negative charges from each other without the expenditure of relatively enormous amounts of energy. The only way it is possible to keep a sustained flow of charge in a wire is to add electrons to one end of the wire and drain off electrons from the other end as fast as they accumulate. The metal conductor thus remains everywhere electrically neutral, since just as many electrons move into a region per unit time as move out.

Most of the electrons that make up the electron cloud of a metal are of very high kinetic energy. Metallic conductivity would therefore be extremely high were it not for a *resistance* effect. Electric resistance is believed to arise because lattice ions vibrate about their lattice points. By interfering with the migration of electrons, the ions keep the conductivity down. At higher temperatures, the thermal vibrations of the lattice increase, and therefore it is not surprising to find that, as the temperature of a metal is raised, its conductivity diminishes.

In solutions, the mechanism of conductivity is complicated by the fact that the positive carriers are also free to move. As pointed out in Sec. 10.4, solutions of electrolytes contain positive and negative ions. There are no free electrons in aqueous solutions. The ions are not fixed in position but are free to roam throughout the body of the solution. When an electric field

14.1 Electric Conductivity

is applied to such a solution, the ions experience a force in one direction in the opposite direction. The ions in opposite directions would stop if positive ions accumulate at the positive electrode; to continue, appropriate chemical reactions maintain electrical neutrality.

That ions migrate when an electric field is applied is seen from the experiment described above. A beaker half filled with a deep-purple solution of $\text{Cu}(\text{MnO}_4)_2$. The solution contains MnO_4^- ions. A colorless aqueous solution of Na^+ ions is poured on top of the $\text{Cu}(\text{MnO}_4)_2$ so that the solution is divided into two layers. The solution by the two electrodes is marked *A*, suggesting a migration of the purple color characteristic of MnO_4^- ions. After some time, the purple color characteristic of MnO_4^- ions has migrated to the positive electrode, marked *B*, indicating that negative ions migrate toward the positive electrode.

As in the case of metal conductors, the electric field is served in all regions of the solution. The conductivity decreases. Figure 14.3 shows that electrical neutrality can be preserved for a solution. A Na^+ ion enters the region of the solution where the charge of the departing Na^+ ion is lost.

Fig. 14.2 Migration of ions in electrolytic conductivity.

Fig. 14.1 Electric forces on ions in solution.

is applied to such a solution, as shown in Fig. 14.1, the positive ions experience a force in one direction, while the negative ions experience a force in the opposite direction. The simultaneous motion of positive and negative ions in opposite directions constitutes the *electrolytic current*. The current would stop if positive ions accumulated at the negative electrode and negative ions at the positive electrode. In order that the electrolytic current continue, appropriate chemical reactions must occur at the electrodes to maintain electrical neutrality.

That ions migrate when electrolytic solutions conduct electricity can be seen from the experiment diagramed in Fig. 14.2. The U tube is initially half filled with a deep-purple aqueous solution of copper permanganate, $\text{Cu}(\text{MnO}_4)_2$. The solution contains blue hydrated Cu^{++} ions and purple MnO_4^- ions. A colorless aqueous solution of nitric acid, HNO_3 , is floated on top of the $\text{Cu}(\text{MnO}_4)_2$ solution. An electric field is maintained across the solution by the two electrodes. After some time, it is observed that the blue color characteristic of hydrated Cu^{++} ions has moved into the region marked *A*, suggesting a migration toward the negative electrode. At the same time, the purple color characteristic of MnO_4^- has moved into the region marked *B*, indicating that negative ions move simultaneously toward the positive electrode.

As in the case of metallic conduction, electric neutrality must be preserved in all regions of the solution at all times. Otherwise, the current soon ceases. Figure 14.3 shows two of the possible ways by which electrical neutrality can be preserved for a given region of a NaCl solution. In (a), one Na^+ ion enters the region defined by the dotted line to compensate for the charge of the departing Na^+ ion. In (b), as one Na^+ ion leaves the region,

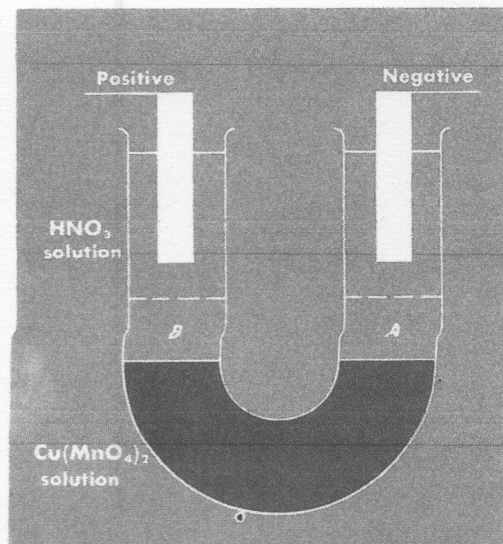


Fig. 14.2 Migration of ions in electrolytic conductivity.

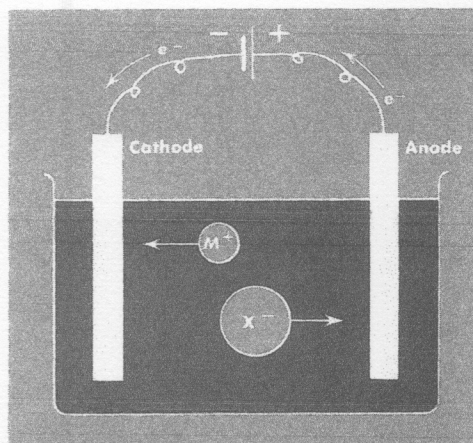
ions and molten salts. In the latter, *electrolytic*. The latter is supplied by a battery or region of space in which there

consist of ordered arrays of atoms. For example, silver consists of a regular pattern with the entire lattice structure determined by the number of Ag^+ ions. The electrons are less fixed in positions from atom to atom. The electrons of the lattice are free to move throughout the crystal. When an electric field is applied, the electrons migrate and thereby conduct electricity. In principle, it should be possible to separate positive and negative ions without the expenditure of relatively small energy. It is possible to keep a positive ion at one end of the wire as they accumulate. The wire remains electrically neutral, since just as positive ions move out.

The free electron cloud of a metal are therefore free to move. Electric resistance is because of their lattice points. By applying an electric field, we can keep the conductivity constant as the lattice increase, and the temperature of a metal

is complicated by the fact pointed out in Sec. 10.4, that positive ions. There are no positive ions of fixed in position but they move. When an electric field

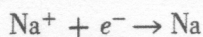
Fig. 14.4 Electrolysis.



trons are crowded onto the left-hand electrode and drained away from the right-hand electrode. The circuit is not complete unless there is some way by which electrons can be used up at the left electrode and formed at the right electrode. Chemical changes must occur. At the left electrode, a *reduction* process must occur in which some ion or molecule accepts electrons and is thereby reduced. The electrode at which reduction occurs is always called a *cathode*. At the right-hand electrode, electrons must be released by an ion or molecule to the electrode. An *oxidation* process must occur. The electrode at which oxidation occurs is always called an *anode*. In order for the reduction process to continue at the cathode, ions must keep moving toward it. These ions are the positive ions and are called *cations*. Simultaneously, negative ions move to the anode and are called *anions*.

14.3 ELECTROLYSIS OF MOLTEN NaCl

Molten NaCl contains Na^+ and Cl^- ions which are free to migrate. Figure 14.5 shows a schematic diagram of the electrolysis cell. Inert electrodes of carbon or platinum dip into the molten NaCl. As diagramed, a reduction process must occur at the left-hand electrode, which therefore is the cathode. Of the two ions, Na^+ and Cl^- , only Na^+ can be reduced. On electrolysis, Na^+ is reduced and forms metallic Na. The *cathode reaction* can be written



indicating that at the cathode one Na^+ ion picks up an electron to form a neutral Na atom. During the change, mass and charge are conserved, so the cathode reaction is in a sense a chemical reaction expressible by a bal-

n; hence the region shows no
cur simultaneously, their rela-
nabilities of the positive and

duction is usually increased
* The difference arises from
ons are already of such high
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14.4. The two vertical lines
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shown by the arrows. Elec-

re exceptions to this generalization.
with some weak electrolytes, the
ciation (Sec. 10.5) may decrease
perature. The decrease in the con-
ons may be big enough to cause a
ductivity.

Two ways that migrating
maintain electric neutrality
of solution.

Fig. 14.5 Electrolysis of molten NaCl.

14.4 ELECTROLYSIS OF AQUEOUS NaCl

When an aqueous NaCl solution is electrolyzed under appropriate conditions, it is observed that hydrogen gas is liberated at the cathode and that chlorine gas is liberated at the anode. How can these observations be accounted for in terms of electrode reactions? Figure 14.6 shows the electrolysis cell, which now contains, besides Na^+ and Cl^- ions, H_2O molecules and traces of H^+ and OH^- from the dissociation of water. Molecules of H_2O can be either oxidized to O_2 and H^+ by removal of electrons or reduced to H_2 and OH^- by the addition of electrons. The H_2O must thus be considered as a possible reactant at each electrode.

At the cathode, reduction must occur. Three different reactions are possible:



It is not easy to predict which of several possible reactions will occur at a cathode. It is necessary to consider which reactant is reduced most *easily* and which reactant is reduced most *rapidly*. The strongest oxidizing agent is not necessarily the fastest. Further complications appear when currents are very large and when concentrations of reactants are very small. The fact that hydrogen gas and not metallic sodium is formed in the electrolysis

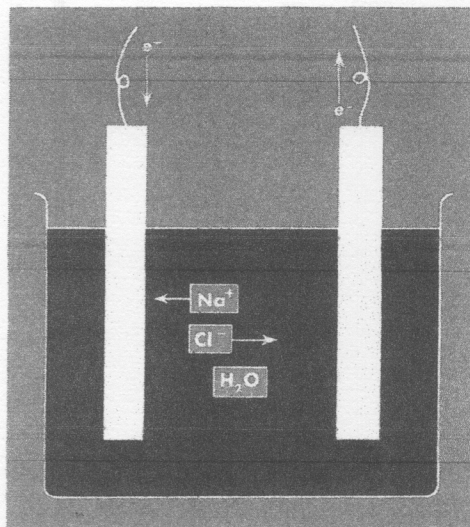
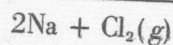


Fig. 14.6 Electrolysis of aqueous NaCl.

ly a reduction process, it is

two species in the cell, Na^+ oxidized, Cl^- releases an electron forms. Two such chlorine atoms form a chlorine molecule, Cl_2 . The net *anode half-reaction* can

sed to convert Na^+ into Na. In addition, the two electrode reactions must disappear at the overall *cell reaction*. In order to balance the half-reactions, the half-reactions must be multiplied so that, when the half-reactions are added, the electrons cancel. Thus, for



the consumption of electrons is shown under the arrow.

of aqueous NaCl indicates that reaction (2) or (3) occurs.* In NaCl solution, the concentration of H^+ is not large enough to make reaction (3) reasonable as a *net change*. Therefore, in the electrolysis of aqueous NaCl, reaction (2) is usually written for the cathode reaction. However, in acidic solutions, the concentration of H^+ may be high enough for H^+ to appear in the net electrode reaction. For example, in the electrolysis of aqueous HCl, the cathode reaction is written as Eq. (3).

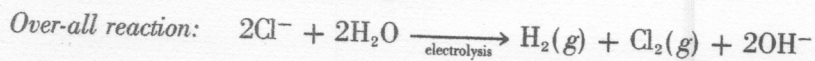
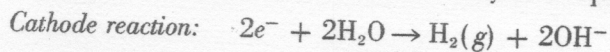
In the electrolysis of NaCl solution, OH^- accumulates in the region around the cathode, and positive ions (Na^+) must move toward the cathode to preserve electric neutrality. In addition, OH^- migrates away from the cathode. Both migrations are consistent with the requirement that cations migrate toward the cathode and anions toward the anode.

At the anode, oxidation must occur. Two different reactions are possible.



In agreement with experiment, reaction (4) is preferred. As the chloride-ion concentration around the anode is depleted, fresh Cl^- moves into the region and Na^+ moves out.

In summary, the equations for the electrolysis of aqueous NaCl are:



As expressed by the over-all reaction, during the electrolysis H_2 gas and Cl_2 gas are formed, the concentration of Cl^- diminishes, and the concentration of OH^- increases. Since there is always Na^+ in the solution, the solution is gradually converted, as time goes on, from aqueous NaCl to aqueous NaOH. In fact, in the commercial production of chlorine by the electrolysis of aqueous NaCl, solid NaOH is obtained as a by-product by evaporating H_2O from the residual solution left after electrolysis.

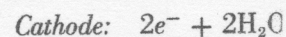
14.5 ELECTROLYSIS OF AQUEOUS Na_2SO_4

When aqueous Na_2SO_4 is electrolyzed, H_2 gas is formed at the cathode, and O_2 is formed at the anode. Changes at the electrodes can be demonstrated

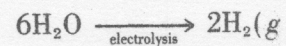
* Years ago it was thought that the metal Na was first formed by reaction (1) and then subsequently reacted with water to liberate H_2 . However, there is no evidence that any intermediate Na is ever formed in this electrolysis.

14.5 Electrolysis of Aqueous

by running the electrolysis in litmus are initially added to contains Na^+ , SO_4^{--} , and F takes the usual violet color while, the litmus in the cathode solution to be basic; the litmus indicating the solution to be the following electrode reaction



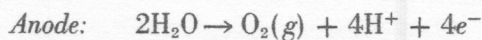
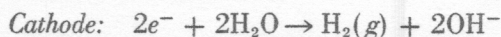
The OH^- from the cathode anode reaction turns litmus doubling the cathode reaction electrons cancel, and the reaction



In this equation, both H^+ and neutralization does not occur in the compartment and OH^- in the compartment poured from the cell in order

Fig. 14.7 Two-compartment electrolysis cell.

by running the electrolysis in the cell shown in Fig. 14.7. A few drops of litmus are initially added to the solution. Before electrolysis, the solution contains Na^+ , SO_4^{--} , and H_2O . It is essentially neutral; therefore litmus takes the usual violet coloration. After electrolysis has proceeded for a while, the litmus in the cathode compartment becomes blue, indicating the solution to be basic; the litmus in the anode compartment becomes red, indicating the solution to be acidic. Consistent with these observations are the following electrode reactions:



The OH^- from the cathode reaction turns litmus blue; the H^+ from the anode reaction turns litmus red. The over-all cell reaction is obtained by doubling the cathode reaction and adding to the anode reaction. The four electrons cancel, and the result is



In this equation, both H^+ and OH^- appear as products. The only reason neutralization does not occur is that the H^+ is formed in the anode compartment and OH^- in the cathode compartment. If the solution is now poured from the cell in order that mixing may take place, neutralization

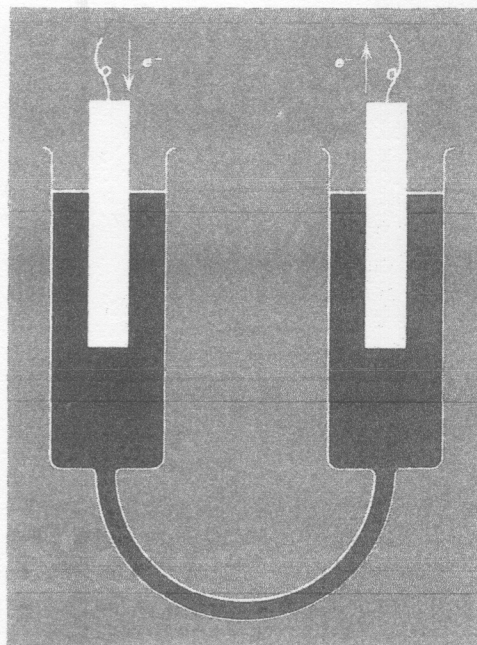
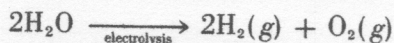


Fig. 14.7 Two-compartment electrolysis cell.

occurs, and the litmus is restored to its original purple color. Addition of the neutralization reaction

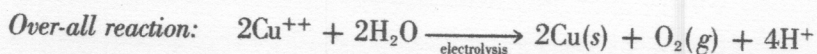
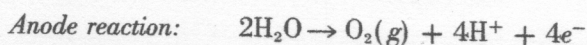
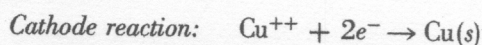


to the above over-all cell reaction gives for the net reaction



In this electrolysis, only water disappears. The Na^+ and SO_4^{--} initially present are also present at the conclusion of the electrolysis. Is the Na_2SO_4 necessary? Because of the requirements of electrical neutrality, some kind of electrolytic solute must be present. Positive ions must be available to move into the cathode region to counterbalance the charge of the OH^- produced. Negative ions must be available to move to the anode to counterbalance the H^+ produced.

Almost any ionic solute makes possible the electrolysis of water as described by the above equations. The only requirement is that the ions of the solute not be oxidized or reduced, as would happen, for example, when aqueous CuSO_4 is electrolyzed. Cu^{++} is more easily and rapidly reduced than H_2O . During electrolysis, copper plating forms on the cathode. The reactions are:

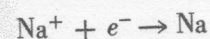


In some cases, the electrodes themselves may take part in the electrode reactions. In each of the above cells, the electrodes were assumed to be inert. This would almost always be the case if the electrodes were made of the inert metal platinum. If, however, the electrode material is reactive, it must be considered as a possible reactant. For example, copper anodes are frequently themselves oxidized during electrolysis when no other species present is more readily oxidized.

14.6 QUANTITATIVE ASPECTS OF ELECTROLYSIS

By experimentation, Michael Faraday, the great English chemist and physicist, established early in the nineteenth century the laws of electrolysis that bear his name (Sec. 3.1). These laws state that the weight of substance produced at an electrode is proportional to the amount of electricity trans-

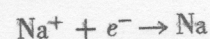
ferred at the electrode and to Faraday's laws can be accounted. For example, in the electrolysis:



tells that one sodium atom is ion disappears and one electron of electrons is transferred, of Na is formed. For this reaction hence transfer of the Avogadro Na. Doubling the amount of sodium produced.

The Avogadro number of amount of electricity that it is In electrical units 1 faraday is described in Appendix 4.7, a c that is transferred when a cu: remember that the current in equal to the number of coulombs by 96,500 is equal to the number

Electrode half-reactions read in terms of moles and faradays. Thus,



can be read either "one sodium atom" or "1 mole of to form 1 gram-atom of sodium"

Example 1

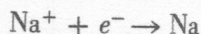
How many grams of chlorine current of 10.0 amp. for 5.00

Coulombs = amperes >

$$\text{Faradays} = \frac{3,000}{96,500} =$$

Since $2\text{Cl}^- \rightarrow \text{Cl}_2(g) +$
2 faradays of elect
0.0311 faraday of
0.0156 mole of Cl

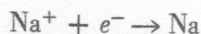
ferred at the electrode and to the gram-equivalent weight of the substance. Faraday's laws can be accounted for by considering the electrode reactions. For example, in the electrolysis of molten NaCl, the cathode reaction



tells that one sodium atom is produced at the electrode when one sodium ion disappears and one electron is transferred. When the Avogadro number of electrons is transferred, 1 mole of Na^+ disappears, and 1 gram-atom of Na is formed. For this reaction, 1 gram-equivalent of Na is 22.991 g.; hence transfer of the Avogadro number of electrons liberates 22.991 g. of Na. Doubling the amount of electricity transferred doubles the weight of sodium produced.

The Avogadro number of electrons is such a convenient measure of the amount of electricity that it is designated by a special name, the *faraday*. In electrical units 1 faraday is equal to 96,500 coulombs of charge. As described in Appendix 4.7, a *coulomb* of charge is the amount of electricity that is transferred when a current of 1 amp. flows for 1 sec. It is useful to remember that the current in amperes multiplied by the time in seconds is equal to the number of coulombs. The electric charge in coulombs divided by 96,500 is equal to the number of faradays.

Electrode half-reactions expressed in ions, electrons, and atoms can be read in terms of moles and gram-atoms if the electricity is expressed in faradays. Thus,



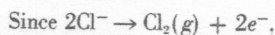
can be read either "one sodium ion reacts with one electron to form one sodium atom" or "1 mole of sodium ions reacts with 1 faraday of electricity to form 1 gram-atom of sodium."

Example 1

How many grams of chlorine can be produced by the electrolysis of molten NaCl at a current of 10.0 amp. for 5.00 min.?

$$\text{Coulombs} = \text{amperes} \times \text{seconds} = 10.0 \times 5.00 \times 60 = 3,000$$

$$\text{Faradays} = \frac{3,000}{96,500} = 0.0311$$



2 faradays of electricity produce 1 mole of Cl_2

0.0311 faraday of electricity produces 0.0156 mole of Cl_2

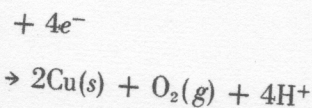
0.0156 mole of Cl_2 weighs $(0.0156)(70.9)$, or 1.11. g.

inal purple color. Addition of

e net reaction

The Na^+ and SO_4^{--} initially
ie electrolysis. Is the Na_2SO_4
ctrical neutrality, some kind
ie ions must be available to
the charge of the OH^- pro-
ve to the anode to counter-

electrolysis of water as de-
irement is that the ions of
happen, for example, when
easily and rapidly reduced
forms on the cathode. The



take part in the electrode
were assumed to be inert.
trodes were made of the
aterial is reactive, it must
e, copper anodes are fre-
n no other species present

ELECTROLYSIS

t English chemist and
the laws of electrolysis
the weight of substance
unt of electricity trans-

Example 2

A current of 0.0965 amp. is passed for 1,000 sec. through 50.0 ml. of 0.100 M NaCl. What will be the average concentration of OH⁻ in the final solution?

$$\text{Faradays} = \frac{(0.0965)(1,000)}{96,500} = 0.00100$$

At the cathode $2e^- + 2H_2O \rightarrow H_2(g) + 2OH^-$

2 faradays liberate 2 moles of OH⁻

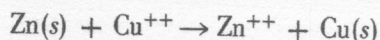
0.00100 faraday liberates 0.00100 mole of OH⁻

In the final solution, assuming the volume is still 50.0 ml., the concentration of OH⁻ is 0.00100 mole per 50.0 ml., or 0.0200 M.

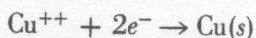
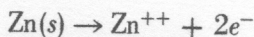
14.7 GALVANIC CELLS

In the above cells, electric energy in the form of a current was used to bring about oxidation-reduction reactions. It is also possible to do the reverse, i.e., use an oxidation-reduction reaction to produce electric current. The main requirement is that the oxidizing and reducing agents be kept separate from each other so that electron transfer must occur through a wire. Any device which accomplishes this is called a *galvanic*, or *voltaic*, cell after Luigi Galvani (1780) and Alessandro Volta (1800), who made the basic discoveries.

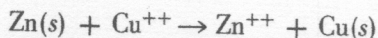
When a bar of zinc is dipped into a solution of copper sulfate, CuSO₄, copper plating is obtained. The net reaction is



In this change, Zn is oxidized and Cu⁺⁺ is reduced, presumably by the direct transfer of electrons from zinc atoms to copper ions. To emphasize this transfer of electrons, the net reaction can be split into two half-reactions:



The galvanic cell operates on the principle that two separated half-reactions can be made to take place simultaneously, with the electron transfer occurring through a wire. The typical galvanic cell shown in Fig. 14.8 uses the reaction



Any galvanic cell that uses this reaction is called a *Daniell cell*. The dotted line represents a porous partition which separates the container into two compartments but still permits diffusion of ions between them. In the left-

14.7 Galvanic Cells

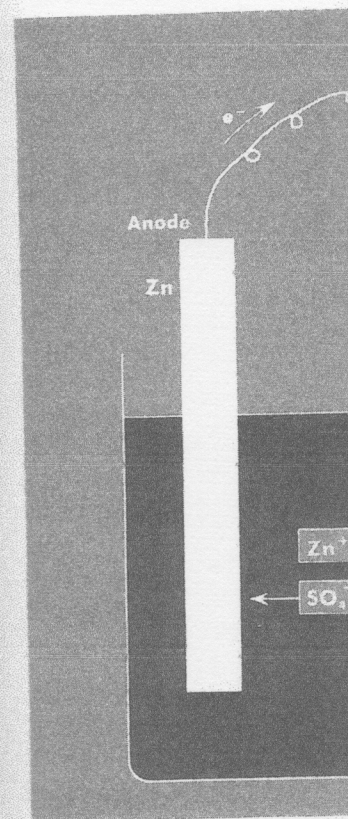
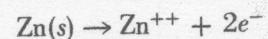


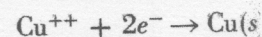
Fig. 14.8 Typical galvanic cell

hand compartment is a solution of zinc sulfate; in the right-hand compartment is a solution of copper sulfate. When the zinc bar is dipped into the solution, the zinc bar is eaten away, and copper is deposited on the bar.

The cell operates as follows. The zinc bar is the anode. The half-reaction



produces Zn⁺⁺ ions and electrons. The Zn⁺⁺ ions are carried into the solution, and the electrons are carried to the copper sulfate compartment where they are picked up by the copper ions.



Copper ions in the solution are reduced to copper metal.

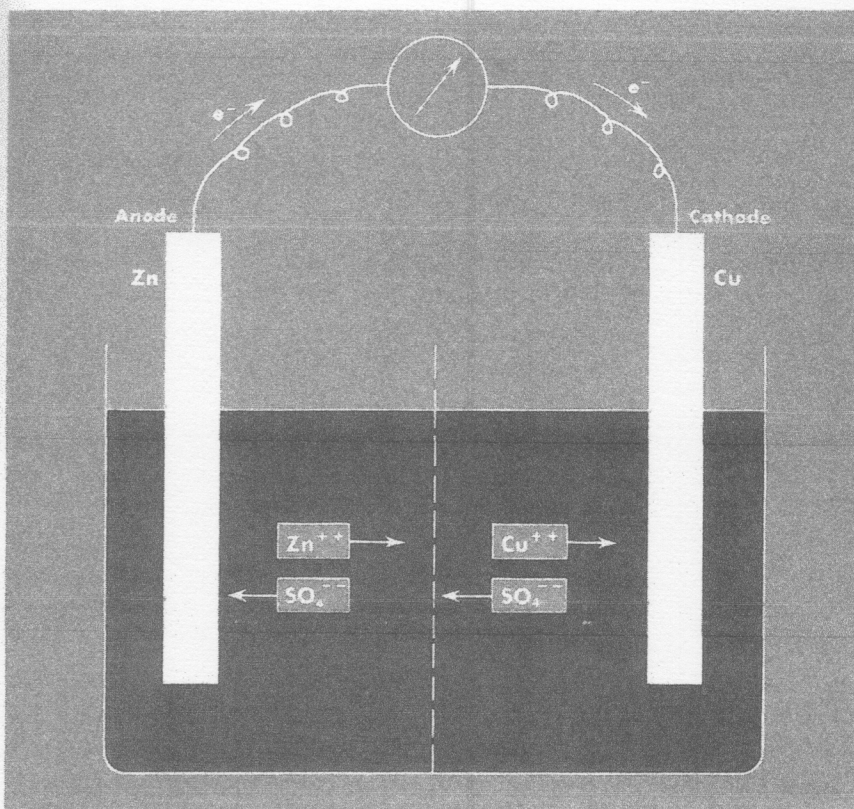
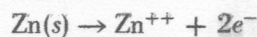


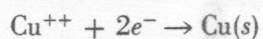
Fig. 14.8 Typical galvanic cell.

hand compartment is a solution of zinc sulfate, into which a zinc bar is dipped; in the right-hand compartment is a copper bar dipping into a solution of copper sulfate. When the two electrodes are connected by a wire, electric current flows, as shown by a meter in the circuit. As time progresses, the zinc bar is eaten away, and copper plates out on the copper bar.

The cell operates as follows: At the zinc bar, oxidation occurs, making Zn the anode. The half-reaction



produces Zn^{2+} ions and electrons. The zinc ions migrate away from the anode into the solution, and the electrons move through the wire, as indicated in the figure. At the copper bar, reduction occurs, making Cu the cathode. The electrons come through the wire and move onto the cathode, where they are picked up and used in the reaction



Copper ions in the solution are depleted, and new copper ions move into

through 50.0 ml. of 0.100 M NaCl.
the final solution?

of OH^{-}
still 50.0 ml., the concentration of
0.0200 M.

if a current was used to bring
possible to do the reverse, i.e.,
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Daniell cell. The dotted
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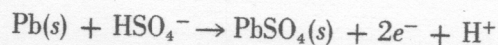
the vicinity of the cathode. The circuit is complete. Consistent with previous notation, cations (Zn^{++} and Cu^{++}) in the solution move toward the cathode (the copper bar), and anions (SO_4^{--}) move toward the anode (the zinc bar). Electrons flow through the wire, and a current is obtained from an oxidation-reduction reaction. The cell runs until either the Zn or Cu^{++} is depleted.

In describing the operation of a galvanic cell, it is not necessary to specify the relative charges of the electrodes. In fact, a simple assignment of charges to the electrodes will not account for the direction of both electron and ion currents. To account for the *electron current* (from anode to cathode in the wire), the anode must be labeled *negative* with respect to the cathode. To account for the *ion current* (negative ions to the anode and positive ions to the cathode), the anode must be labeled *positive* with respect to the cathode. How can the anode be positive and negative at the same time? The discrepancy is resolved by considering the electrode in detail. For example, at the Daniell cell anode, Zn^{++} is produced. These Zn^{++} ions form a layer which makes the anode appear positive as viewed from the solution. The electrons released in forming Zn^{++} make the anode appear negative as viewed from the wire.

Actually, to get a current from a Daniell cell, the Zn^{++} ions and the Cu bar need not be initially present. Any metal support for the plating of Cu will do in place of the Cu bar. Any positive ion that does not react with Zn metal will do in place of Zn^{++} . However, as the cell reaction proceeds, Zn^{++} is necessarily produced at the anode. Furthermore, the porous partition is necessary only to keep Cu^{++} from easily getting over to the Zn metal, where direct electron transfer would short-circuit the cell. The partition must be porous in order to allow the diffusion of positive and negative ions from one compartment to the other. Otherwise the solution would soon become positively charged in the anode compartment (due to accumulation of Zn^{++}) and negatively charged in the cathode compartment (due to depletion of Cu^{++}), causing the current to cease.

In principle, any oxidation-reduction reaction is separable into two half-reactions and can be made a source of electric current as a galvanic cell. Probably the most famous example is the *lead storage battery*, or *accumulator*. As shown in Fig. 14.9, the basic features are electrodes of lead, Pb, and lead dioxide, PbO_2 , dipping into aqueous H_2SO_4 . When the cell operates, the reactions are:

Anode:



Cathode:

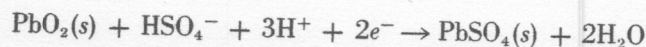
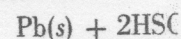


Fig. 14.9 Cell of a lead storage battery.

Over-all cell reaction:



The insoluble lead sulfate, PbSO_4 , plates to the electrode. During the discharge, the electrodes are reversed so as to restore the original state, as shown by the over-all cell reaction. The concentration of H_2SO_4 in the electrolyte solution is chiefly dependent on the state of charge. The density of the solution tells how far the cell is discharged.

Another common galvanic cell is the *dry cell*. The cell consists of a zinc anode surrounded by a moist paste of MnO_2 , ZnCl_2 , and ammonium chloride. The graphite rod is the cathode. MnO_2 is reduced. The electromotive force varies to vary, depending on how far the cell is discharged. The delivery of very small currents is possible.

Anode:

Cathode:

Over-all cell reaction:

* It would seem natural to say that the anode is positive and the cathode is negative. However, as is obvious from the cell reaction, the anode is the cathode in order to form PbSO_4 . Thus, the current flows toward both electrodes.

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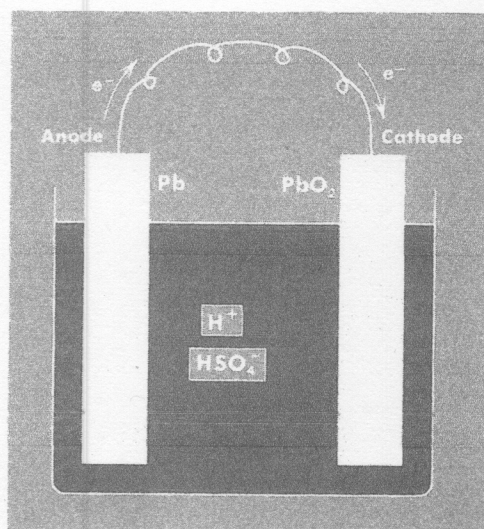
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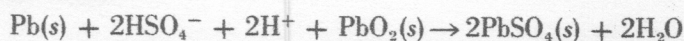
+ H^+

$PbSO_4(s) + 2H_2O$

Fig. 14.9 Cell of a lead storage battery.

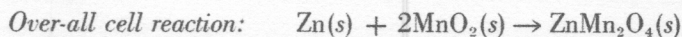
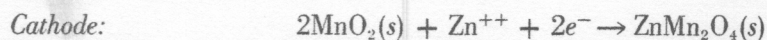


Over-all cell reaction:



The insoluble lead sulfate, $PbSO_4$, that is formed at each electrode adheres to the electrode. During the *charging* of a battery, the electrode reactions are reversed so as to restore the cell to its original condition. In *discharge*, as shown by the over-all cell reaction, Pb and PbO_2 are depleted, and the concentration of H_2SO_4 is diminished. Since the density of the aqueous solution is chiefly dependent on the concentration of H_2SO_4 , measurement of the density tells how far the cell is discharged.*

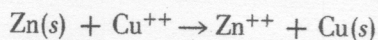
Another common galvanic cell is the Leclanché dry cell used in flashlights. The cell consists of a zinc can containing a centered graphite rod surrounded by a moist paste of manganese dioxide, MnO_2 , zinc chloride, $ZnCl_2$, and ammonium chloride, NH_4Cl . The zinc can is the anode, and the graphite rod is the cathode. At the anode, Zn is oxidized; at the cathode, MnO_2 is reduced. The electrode reactions are extremely complex and seem to vary, depending on how much current is drawn from the cell. For the delivery of very small currents, the following reactions are probable:



* It would seem natural to say that, when the battery is discharging, the anion HSO_4^- moves to the anode. However, as is obvious from the cathode half-reaction, some of the HSO_4^- must also move to the cathode in order to form $PbSO_4$. Thus we have the unusual but not unique situation that the anion moves toward both electrodes.

14.8 OXIDATION POTENTIALS

A voltmeter connected between the two electrodes of a galvanic cell shows a characteristic voltage which depends in magnitude on what reactants take part in the electrode reactions and on what their concentrations are. For example, in the Daniell cell, if Zn^{++} and Cu^{++} are at 1 *m* concentration, and the temperature is 25°C., the voltage measured between the Zn electrode and the Cu electrode is 1.10 volts, no matter how big the cell or how big the electrodes. This voltage is characteristic of the Daniell cell reaction



The voltage measures the force with which electrons are moved around the circuit and therefore measures the tendency of this reaction to take place. Thus, galvanic cells give a quantitative measure of the relative tendency of various oxidation-reduction reactions to occur.

Figure 14.10 shows a galvanic cell set up to study the reaction

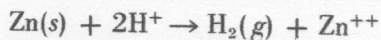


Fig. 14.10 Voltage measurement of zinc-hydrogen cell.

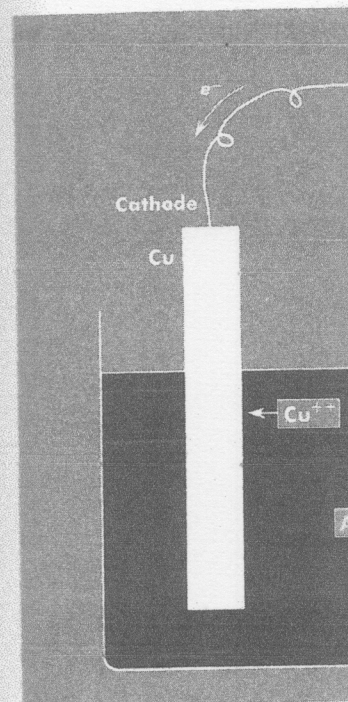
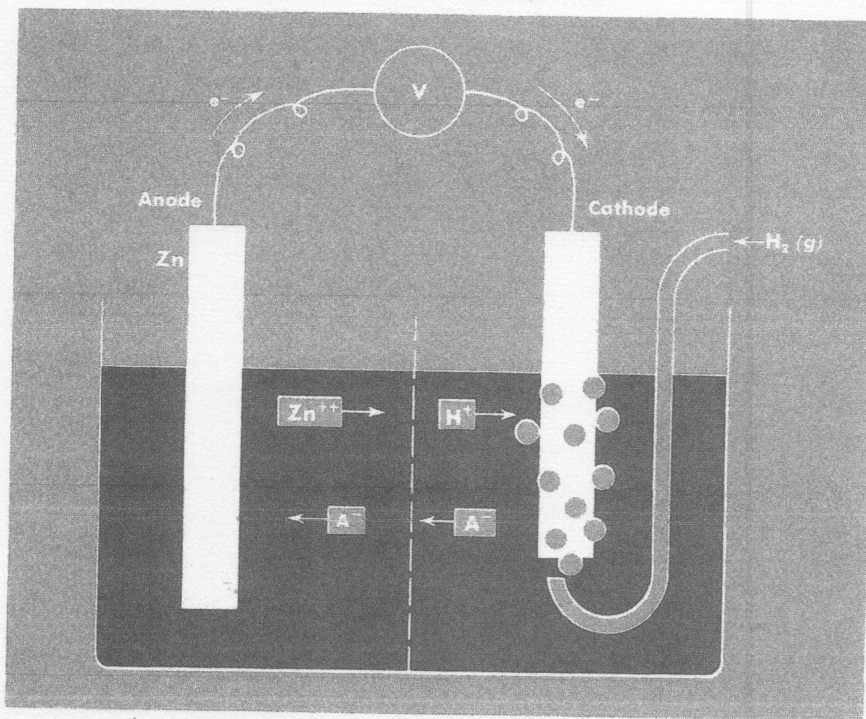
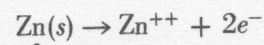
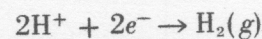


Fig. 14.11 Voltage measurement

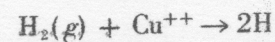
In the anode compartment, $\text{Zn}(s)$ is oxidized to Zn^{++} . In the cathode compartment, H^+ is reduced to H_2 over an inert electrode, made of platinum. The anode reaction is



The cathode reaction is



When the concentrations of Zn^{++} and H^+ are 1 *m* and the pressure of the H_2 gas is 1 atm., the deflection is in such direction as to give off electrons. The cell potential for the reaction $\text{Zn}(s) \rightarrow \text{Zn}^{++} + 2e^-$ is 0.76 volt. The galvanic cell in Figure 14.10 is



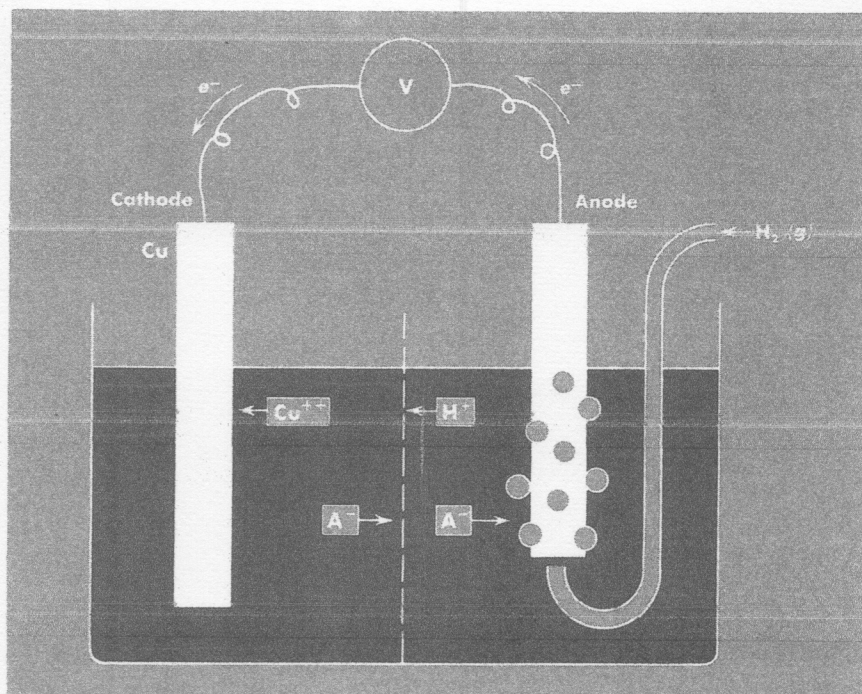
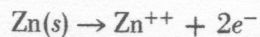
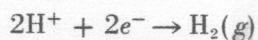


Fig. 14.11 Voltage measurement of copper-hydrogen cell.

In the anode compartment, a zinc bar dips into a solution of a zinc salt. In the cathode compartment, H_2 gas is led in through a tube so as to bubble over an inert electrode, made, for example, of Pt, dipped into an acidic solution. The anode reaction is

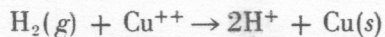


The cathode reaction is



When the concentrations of H^+ and of Zn^{++} are 1 *m* and when the pressure of the H_2 gas is 1 atm., the voltmeter reads 0.76 volt (at 25°C.), and the deflection is in such direction as to indicate that Zn has a greater tendency to give off electrons than has H_2 . In other words, the half-reaction $Zn(s) \rightarrow Zn^{++} + 2e^-$ has a greater tendency to occur than $H_2(g) \rightarrow 2H^+ + 2e^-$ by 0.76 volt.

The galvanic cell in Fig. 14.11 makes use of the reaction

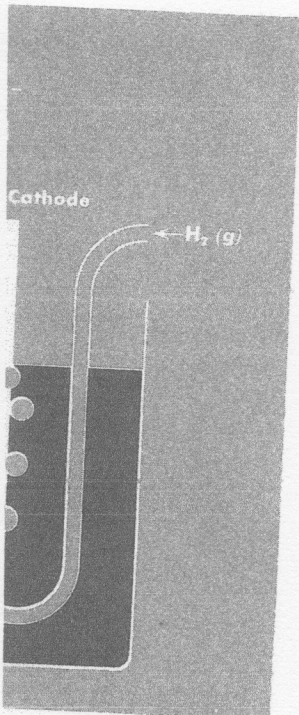


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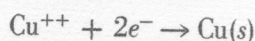
ell.



The anode reaction is



and the cathode reaction is



When the concentrations of H^+ and Cu^{++} are 1 *m* and when the pressure of H_2 is 1 atm., the voltmeter reads 0.34 volt (at 25°C.), and the direction indicates that H_2 has a greater tendency to give off electrons than has Cu. In other words, the half-reaction $\text{H}_2(g) \rightarrow 2\text{H}^+ + 2e^-$ has a greater tendency to occur than $\text{Cu}(s) \rightarrow \text{Cu}^{++} + 2e^-$ by 0.34 volt.

In all cells, the voltage observed arises from two sources: a voltage at the anode and a voltage at the cathode. If either of these voltages were known, the other could be obtained by subtraction. However, it is impossible to measure the voltage of an individual electrode, since any complete circuit necessarily contains two electrodes. We are forced to assign a completely arbitrary voltage to one electrode. The voltage of the other electrode is thereby fixed. For convenience, the voltage of the standard hydrogen electrode (at 25°C., 1 atm. H_2 pressure, and 1 *m* H^+ concentration) is given the value zero. Consequently, in any cell which contains the hydrogen electrode, the entire measured voltage is attributed to the half-reaction at the other electrode. Voltages thus assigned are called *oxidation potentials*.

Table 14.1 lists various half-reactions with their oxidation potentials. A more extensive listing is given in Appendix 7. The double arrows indicate that under appropriate conditions the half-reaction can be made to go in either direction. The voltage given applies when the half-reaction proceeds in the forward direction. For the reverse direction, the sign of the voltage must be changed.

The forward reaction is an oxidation in which the reducing agent, shown on the left, is oxidized. The table is so arranged that the reducing agents are listed in order of decreasing strength. In other words, there is decreasing tendency of the forward half-reaction to occur from the top of the table to the bottom. For example, of the list given, lithium, Li, is the best reducing agent, since it has the highest tendency to give off electrons. Fluoride ion, F^- , is the worst reducing agent and has the least tendency to give off electrons. Such a list of reducing agents arranged in decreasing order is sometimes called the *electromotive series*.

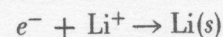
The numerical values of the oxidation potentials given in Table 14.1 apply to aqueous solutions at 25°C. in which the concentration of dissolved species is 1 *m*. A positive value of the oxidation potential indicates that the reducing agent is stronger than H_2 ; a negative value indicates that the re-

Table 14.1 Some Half-reactions

	Half-reaction
Li(s)	$\rightleftharpoons \text{Li}^+$
Na(s)	$\rightleftharpoons \text{Na}^+$
Mg(s)	$\rightleftharpoons \text{Mg}^{++}$
Al(s)	$\rightleftharpoons \text{Al}^{+++}$
Zn(s)	$\rightleftharpoons \text{Zn}^{++}$
Fe(s)	$\rightleftharpoons \text{Fe}^{++}$
$\text{H}_2(g)$	$\rightleftharpoons 2\text{H}^+$
$\text{Cu}(s)$	$\rightleftharpoons \text{Cu}^{++}$
2I^-	$\rightleftharpoons \text{I}_2$
Ag(s)	$\rightleftharpoons \text{Ag}^+$
Hg(l)	$\rightleftharpoons \text{Hg}^{++}$
2Br^-	$\rightleftharpoons \text{Br}_2$
$2\text{H}_2\text{O}$	$\rightleftharpoons \text{O}_2 + 4\text{H}^+$
2Cl^-	$\rightleftharpoons \text{Cl}_2$
$4\text{H}_2\text{O} + \text{Mn}^{++}$	$\rightleftharpoons \text{MnO}_2 + 8\text{H}^+$
2F^-	$\rightleftharpoons \text{F}_2$

ducing agent is weaker than H_2 . The numerical value is a relative measure of the relative tendency to go to the left or to the right. (It should be noted that a reaction is *fast* enough to be measured.)

Each reducing agent in its oxidized form. For example, Li^+ is the oxidized form of Li. Each oxidizing agent is capable of acting as an oxidizing agent by some means. Thus, the formation of Li^+ from Li is a measure of the relative tendency of Li to be oxidized. If a half-reaction, such as $\text{Li} \rightarrow \text{Li}^+ + e^-$, has a greater tendency to go to the right, it is a poor one. Of the oxidizing agents, F_2 is the best. The half-reaction



has a smaller tendency to occur than

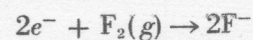


Table 14.1 lists oxidizing agents in order of decreasing strength.

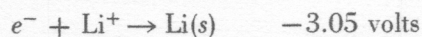
* This assignment of "positive" is in the opposite sense. In fact, most of the values are negative. *Latin: non est disputandum.*

Table 14.1 Some Half-reactions and Their Oxidation Potentials

Half-reaction	Potential, volts
$\text{Li}(s) \rightleftharpoons \text{Li}^+ + e^-$	+3.05
$\text{Na}(s) \rightleftharpoons \text{Na}^+ + e^-$	+2.71
$\text{Mg}(s) \rightleftharpoons \text{Mg}^{++} + 2e^-$	+2.37
$\text{Al}(s) \rightleftharpoons \text{Al}^{++} + 3e^-$	+1.66
$\text{Zn}(s) \rightleftharpoons \text{Zn}^{++} + 2e^-$	+0.76
$\text{Fe}(s) \rightleftharpoons \text{Fe}^{++} + 2e^-$	+0.44
$\text{H}_2(g) \rightleftharpoons 2\text{H}^+ + 2e^-$	0
$\text{Cu}(s) \rightleftharpoons \text{Cu}^{++} + 2e^-$	-0.34
$2\text{I}^- \rightleftharpoons \text{I}_2 + 2e^-$	-0.54
$\text{Ag}(s) \rightleftharpoons \text{Ag}^+ + e^-$	-0.80
$\text{Hg}(l) \rightleftharpoons \text{Hg}^{++} + 2e^-$	-0.85
$2\text{Br}^- \rightleftharpoons \text{Br}_2 + 2e^-$	-1.09
$2\text{H}_2\text{O} \rightleftharpoons \text{O}_2(g) + 4\text{H}^+ + 4e^-$	-1.23
$2\text{Cl}^- \rightleftharpoons \text{Cl}_2(g) + 2e^-$	-1.36
$4\text{H}_2\text{O} + \text{Mn}^{++} \rightleftharpoons \text{MnO}_4^- + 8\text{H}^+ + 5e^-$	-1.51
$2\text{F}^- \rightleftharpoons \text{F}_2(g) + 2e^-$	-2.87

ducing agent is weaker than H_2 . * The magnitude of the potential is a quantitative measure of the relative tendency of the half-reaction to occur from left to right. (It should be noted that nothing is implied about whether the reaction is *fast* enough to be observed.)

Each reducing agent in Table 14.1 is coupled in its half-reaction with its oxidized form. For example, Cu is coupled with Cu^{++} . The oxidized form is capable of acting as an oxidizing agent when the half-reaction is reversed by some means. Thus, the oxidation potentials in Table 14.1 also give information about the relative tendency of oxidizing agents to pick up electrons. If a half-reaction, such as the one at the top of the table, has great tendency to go to the right, it is hard to reverse, and the oxidizing agent is a poor one. Of the oxidizing agents listed, Li^+ is the poorest, and fluorine, F_2 , the best. The half-reaction



has smaller tendency to occur than

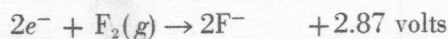
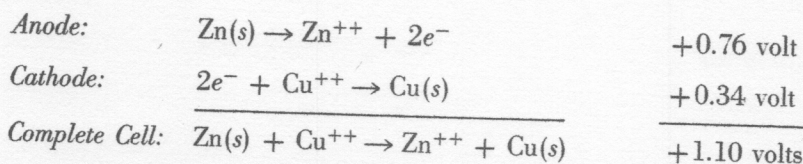


Table 14.1 lists oxidizing agents (on the right) in order of increasing strength.

* This assignment of "positive" and "negative" is arbitrary and could perhaps be better chosen in the opposite sense. In fact, most of the world outside America does use the opposite convention. *De gustibus non est disputandum.*

The voltage of a half-reaction is a measure of the tendency of the half-reaction to occur. This voltage is independent of the other half of the complete reaction. The voltage of any complete reaction can be obtained by addition of the voltages of its two half-reactions. The voltage so obtained gives the tendency of the complete reaction to occur and is the voltage measured for a galvanic cell which uses the reaction. For example, in the Daniell cell:



The voltage, +1.10, so calculated is that observed for the Daniell cell. It is positive, which indicates that the reaction tends to go spontaneously as written. It should be noted that the value 1.10 volts applies when the concentrations of the ions are 1 *m*, since oxidation potentials are defined for concentrations of 1 *m*. If the concentrations are changed, the cell voltage changes, as can be predicted by the Le Chatelier principle. For example, an increase in Cu^{++} concentration means that the reaction has greater tendency to go to the right, and the voltage is increased. Likewise, an increase in Zn^{++} concentration decreases the voltage.*

Any oxidation-reduction reaction for which the voltage is positive has the tendency to take place as written. Whether a given reaction should take place spontaneously can be determined from the relative positions of its two half-reactions in a table of oxidation potentials. In Table 14.1, for example, any reducing agent reacts with any oxidizing agent below it. Zn reduces Fe^{++} , H^+ , Cu^{++} , etc., but does not reduce Al^{+3} , Mg^{++} , Na^+ , etc. Similarly, any oxidizing agent reacts with any reducing agent above it. I_2 oxidizes Cu, H_2 , Fe, etc., but does not oxidize Br^- , H_2O , Cl^- , etc.

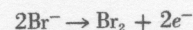
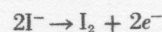
Example 3

I_2 and Br_2 are added to a solution containing I^- and Br^- . What reaction would occur if the concentration of each species were 1 *m*?

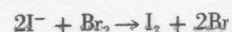
* Actually, the tendency of a reaction to occur is influenced not only by the concentrations of species but also by interionic attractions (Sec. 10.6) and other complicating factors such as the change of hydration with concentration. All of these factors as well as concentration contribute to the effectiveness of a species to take part in the chemical reaction or, in other words, contribute to the *chemical activity* of the species. For precise work, it is the *chemical activity* rather than the *concentration* of the species that must be specified. Strictly speaking, then, the oxidation potentials given in Table 14.1 are defined for all species at unit activity. For our purposes we shall assume that activity can be represented by concentration in terms of molality.

14.9 Balancing Equations by

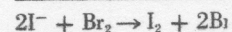
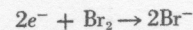
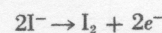
The half-reactions to be co



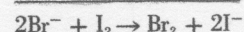
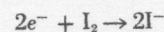
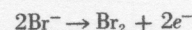
Method (a). From the po cannot reduce I_2 . Therefore, the



Method (b)



Therefore, this reaction should reaction is positive.

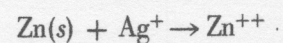


Therefore, this reaction should

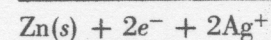
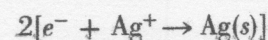
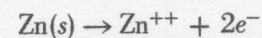
14.9 BALANCING

An oxidation half-reaction r reaction, in order that the e turbed. This requirement of balancing equations which c cussed in Sec. 5.7 in that t longer necessary.

The balanced equation :



can be written by noting that and that these two electron two Ag atoms. The princip and then match electron los



of the tendency of the half-
the other half of the com-
action can be obtained by
s. The voltage so obtained
occur and is the voltage
ation. For example, in the

$$\begin{array}{r} +0.76 \text{ volt} \\ +0.34 \text{ volt} \\ \hline +1.10 \text{ volts} \end{array}$$

ed for the Daniell cell. It
is to go spontaneously as
its applies when the con-
potentials are defined for
changed, the cell voltage
principle. For example, an
reaction has greater tend-
ed. Likewise, an increase

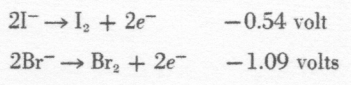
ie voltage is positive has
ven reaction should take
relative positions of its
s. In Table 14.1, for ex-
g agent below it. Zn re-
Al³⁺, Mg²⁺, Na⁺, etc.
ucing agent above it. I₂
H₂O, Cl⁻, etc.

What reaction would occur if

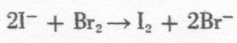
only by the concentrations of
ating factors such as the change
tion contribute to the effective-
rds, contribute to the chemical
er than the concentration of the
entials given in Table 14.1 are
that activity can be represented

14.9 Balancing Equations by Half-Reactions

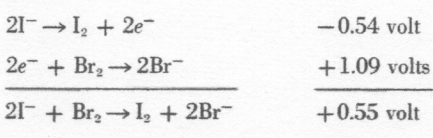
The half-reactions to be considered are



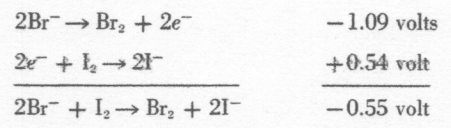
Method (a). From the positions in Table 14.1, I⁻ can reduce Br₂, whereas Br⁻ cannot reduce I₂. Therefore, the reaction is



Method (b)



Therefore, this reaction should occur spontaneously as written, since the voltage for the reaction is positive.

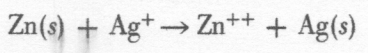


Therefore, this reaction should not occur spontaneously as written.

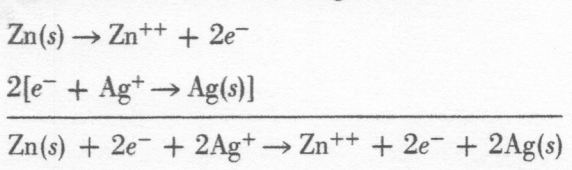
14.9 BALANCING EQUATIONS BY HALF-REACTIONS

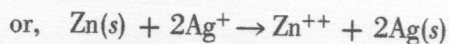
An oxidation half-reaction must always be paired with a reduction half-reaction, in order that the electron balance of the world may not be disturbed. This requirement of electron balance makes possible a method of balancing equations which differs from the oxidation-number method discussed in Sec. 5.7 in that the artificially devised oxidation number is no longer necessary.

The balanced equation for the change

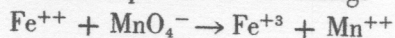


can be written by noting that the Zn must release two electrons to form Zn²⁺ and that these two electrons must be picked up by two Ag⁺ ions to form two Ag atoms. The principle of the method is to write the half-reactions and then match electron loss and gain. Thus,

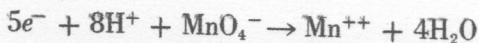
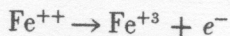




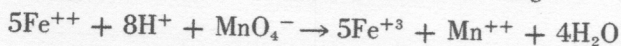
The balanced equation for the change



in acidic solution can be written from the two half-reactions



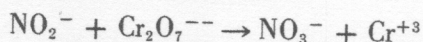
Multiplying the first by 5 and adding to the second gives



When given an equation to balance in acidic solution, the detailed steps to follow are:

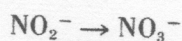
1. Separate the change into half-reactions.
2. Balance each half-reaction separately by:
 - a. Changing coefficients to account for all atoms except H and O.
 - b. Add H_2O to side deficient in O.
 - c. Add H^+ to side deficient in H.
 - d. Add e^- to side deficient in negative charge.
3. Multiply half-reactions by appropriate numbers needed to balance electrons, and add.
4. Subtract any duplications on left and right.

The following example shows the stepwise procedure used to write a balanced equation for the change

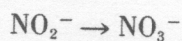


in acidic solution.

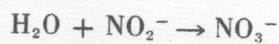
Step (1):



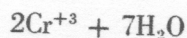
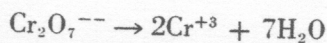
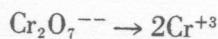
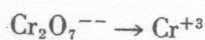
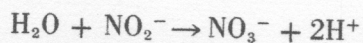
Step (2a):



Step (2b):

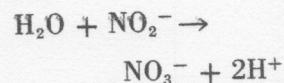


Step (2c):



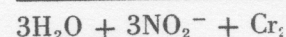
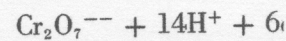
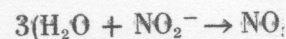
Questions

Step (2d):



[Two electrons have been added to the right side, since in step (1) the left side has a net charge of -1 and the right side has a net charge of +1. The right side was deficient in negative charge by two units.]

Step (3):

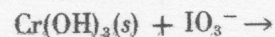


where $3\text{H}_2\text{O}$, 6H^+ , and $6e^-$ cancel.

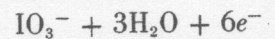
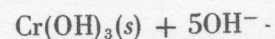
Step (4):



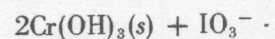
If the reaction occurs in basic solution, H^+ is added to the opposite side of the deficiency of H^+ to the deficiency of the opposite side. The rest of the reaction in basic solution is the same.



The half-reactions are



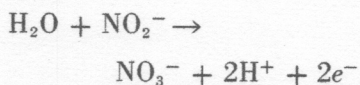
and the final net equation is



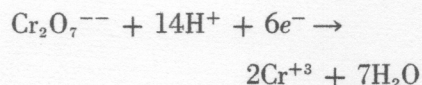
QUESTIONS

14.1 Electrical terms. Distri

Step (2d):

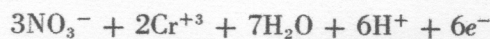
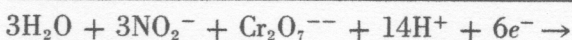
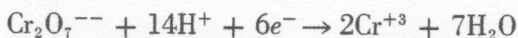


[Two electrons have been added to the right side, since in step (2c) the left side has a net charge of -1 and the right side has a net charge of $+1$. The right side was deficient in negative charge by two units.]



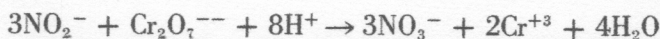
[Six electrons have been added to the left, since in step (2c) the left side is $+12$ while the right side is $+6$.]

Step (3):

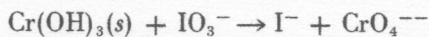


where $3\text{H}_2\text{O}$, 6H^+ , and $6e^-$ are duplicated on left and right.

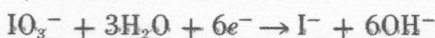
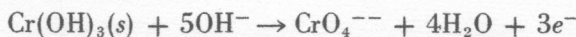
Step (4):



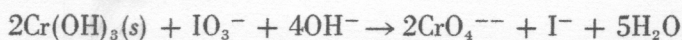
If the reaction occurs in basic solution, the equation must not contain H^+ . In order to add H atoms in step (2c), add H_2O molecules equal in number to the deficiency of H atoms and an equal number of OH^- ions to the opposite side. The rest of the method is the same. An example of a reaction in basic solution is the change



The half-reactions are



and the final net equation is



QUESTIONS

14.1 *Electrical terms.* Distinguish between faraday, coulomb, and ampere.