Ch. 8. Electrochemistry

B ATTERIES are portable power devices, essential in our every day life. They power cellphones and even cars. Batteries use the principles of chemistry to produce electricity. Galvanic cells are textbook batteries, not intended to generate electricity as they function reversibly and in equilibrium. In the eighteenth century, Luigi Galvani discovered that animals' muscles–in particular dead frogs–could be artificially moved by touching the muscles with rods of different metals. The generated electricity at first was believed to come from the muscles. However, Alessandro Volta proved that the source of electricity in muscle movement was indeed the metals. Volta created the first Voltaic pile by stacking metallic silver and zinc disks separated by paper soaked in saltwater. This early discovery jumpstarted electrochemistry, a new field of chemistry. Indeed, chemical reactions can produce electricity, and electricity can drive chemical reactions.

8.1 Introduction to galvanic cells

Galvanic cells–also known as voltaic cells or piles–are electrochemical cells that generate electricity from spontaneous redox reactions. They contain two different metals immersed in electrolyte solutions. Each half-cell contains a metal in contact with a liquid solution of the same metal in ionic form. Both half-cells are either connected by a salt bridge or separated by a porous membrane. Galvanic cells differ from batteries. Batteries are composed of multiple single cells working out of equilibrium while producing electricity. Galvanic cells are textbook batteries. They are reversible devices unable to produce electricity.

Components of a galvanic cell Galvanic cells are composed of two different electrodes, an anode, and a cathode, connected by means of a salt bridge or a membrane. The role of the salt bridge or membrane is to complete the electrical circuit. Anodes are sources of electrons, whereas cathodes are electron sinks. At the same time, anodes generate positive cations, whereas cathodes generate negative anions. The role of the salt bridge or membrane is also to allow the charges generated in the cathode to be compensated by the charges generated in the anode. Electrodes contain two different redox states of the same element in contact with each other. An example of an electrode would be a piece of metallic copper Cu in contact with a solution of $Cu^{2+}_{(aq)}$ ions. However, electrodes are not always made of metals. For example, electrodes can contain gas in contact (e.g. $H_{2(g)}$) with an electrolyte solution (e.g. $H^{+}_{(aq)}$). Electrodes without a metall being directly involved in the redox reaction need to include an external metal to support the charge transfer. Metals such as Pt are normally used for this

purpose.

The electrodes: anode and cathode Every galvanic cell is composed of two electrodes: an anode and a cathode. Electrodes produce ionic and electronic charges. The oxidation occurs on the anode which is indicated with a negative $(-)$ sign. Electrons are being produced in the anode resulting from an oxidation reaction. The reduction occurs on the cathode, indicated with a positive $(+)$ sign. Electrons are being consumed in the cathode resulting from a reduction reaction. These electrodes also produce ions, in particular cations and anions which have a tendency to migrate inside the cell. Anodes generate cations (and consume anions, depending on the chemical reaction involved), whereas cathodes generate anions (and consume cations, again, depending on the chemical reaction involved). As such, anions have a tendency to migrate to the anode, as their concentration is lower there, whereas cations have a tendency to migrate to the cathode. The excess ionic charge is compensated in the interface between the electrode and the salt bridge or the membrane. Mind that in a galvanic cell only electrons flow through the circuit, by means of the wire connecting both electrodes. The ions involved have a tendency to migrate inside each of the electrodes but do not leave the electrode. The name of the electrodes–anode and cathode–results from the ionic flow involved in the galvanic cell: anions have a tendency to migrate towards the anode and cations to the cathode.

Cell potential Water flows down a waterfall due to the difference of potential energy between the high and low parts of the waterfall. Similarly, heat flows between a hot and a cold reservoir due to the difference in temperature between both locations. The force that drives the flow is heat is temperature. Electricity flows through a galvanic cell resulting from the difference of cell potential $\Delta\mathcal{E}$ between both electrodes, the anode, and the cathode. The cell potential–also referred to as cell voltage, cell electromotive force, or cell *emf*–is the force that drives the flow of electrons. Anodes and cathodes have a characteristic cell potential associated with the electrochemical half-reaction happening in the electrode. The voltage of the anode ($\mathcal{E}_{anode}$) is always lower than the one from the cathode ($\mathcal{E}_{cathode}$). The combination of the anodic and cathodic voltage gives the overall cell potential measured in a galvanic cell. In particular, the overall voltage results from the voltage of the cathode with respect to the anode, so that the overall voltage of a galvanic cell is always positive.

Role of the salt bridge or the membrane The role of the salt bridge or the porous membrane is to compensate for the excess of ions generated in each electrode hence closing the electric circuit. Salt bridges contain saturated solutions of electrolytes containing ions with similar ionic mobility (KCl or NH_4NO_3). These electrolytes are also non-reactive with the chemicals involved in the galvanic cell. Each side of the salt bridge or membrane becomes charged due to ionic accumulation, with negative ions accumulating near the cathode and positive charges near the anode. Porous membranes impact the galvanic cell potential with an extra contribution called the liquid junction voltage. This voltage is due to the ion accumulation on both sides of the membrane. When using a salt bridge, the liquid junction voltage on the left side of the bridge compensates the salt bridge on the right side of the bridge so that overall the galvanic cell potential remains unaffected by the bridge.

A galvanic cell example Below we display a representation of the Daniell cell, a classical galvanic cell in which copper is oxidized by zinc. The name of the cell is in honor of John Daniell, a British chemist from the nineteenth century who was trying to develop an electric power supply to sustain telegraphy. He connected with a metallic

3

wire a zinc electrode in contact with a zinc sulfate solution to a copper electrode in contact with a copper (II) sulfate solution. In this cell, Copper(II) ions are converted into metallic copper in the cathode by means of the reaction $Cu^{2+}_{(aq)} + 2\,e^- \longrightarrow Cu_{(s)}$, whereas metallic zinc is converted into zinc ions in the anode following the reaction $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\,e^-$. Copper(II) ions are being reduced whereas zinc is being oxidized. The cathode solution becomes negatively charged whereas the anode solution becomes positively charged. A porous membrane permeable to ions was used to avoid the charge buildup.
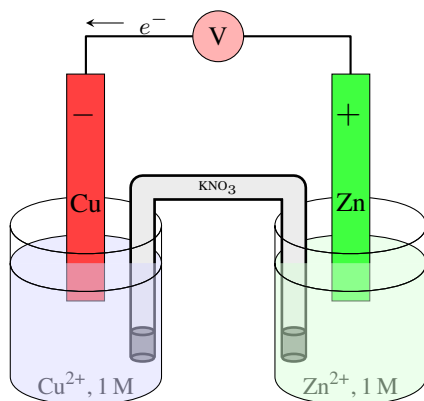

Figure 8.2 The Daniell galvanic cell

The potentiometer Voltmeters are devices used to measure cell potential, the number of Volts, in electric circuits. These devices work by drawing current through a know resistance. Voltmeter can not be used to precisely measure the voltage of a galvanic cell. As electricity flows into the voltmeter, frictional heating will occur and energy will be wasted. Hence the voltage measured would be lower than the real voltage. In order to avoid this problem in a lab setting, we normally use potentiometers to measure galvanic cells. Potentiometers apply a counter-voltage to compensate the cell voltage without drawing any significant current. Due to their high internal resistivity, there is no electricity flow in a voltaic cell connected to a voltmeter. The cell remains in equilibrium, and the electrodes are not consumed. Still, an ammeter could be used to measure the tendency of the cell to generate a measurable intensity flow, the Amperes.

Sample Problem 1

For the galvanic cell below, indicate: (a) label the electrode as anode and cathode (b) identify the flow of electrons (c) identify the flow of cations and anions (d) identify the oxidation and reduction
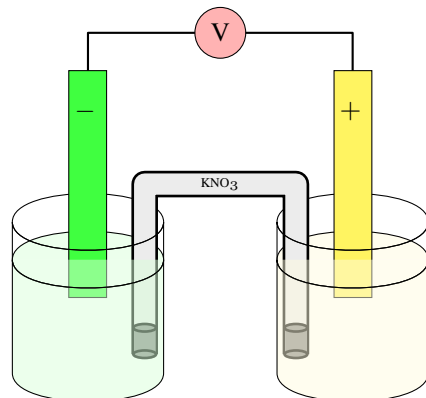
SOLUTION

(a) The electrode labeled with the − sign located on the left is the anode, where the oxidation takes place. Electrons are being produced in the anode and cations are also being generated in the anode (or perhaps anions are being consumed, it depends on the redox reaction happening). The electrode labeled with the + sign located on the right is the cathode, where the reduction takes place. Electrons are consumed in the cathode and anions are also being generated in the cathode. (b) The flow of electrons goes from the anode on the left to the cathode on the right (c) Cations are being produced in the anode and they have a tendency to migrate towards the cathode. Anions are being produced in the cathode and they have a tendency to migrate towards the anode. (d) The oxidation takes place on the anode on the left, whereas the reduction takes place on the cathode on the left.

◈ **STUDY CHECK**

For the galvanic cell below, indicate: (a) label the signs of the electrodes (b) identify the flow of electrons (c) identify the flow of cations and anions (d) identify the oxidation and reduction
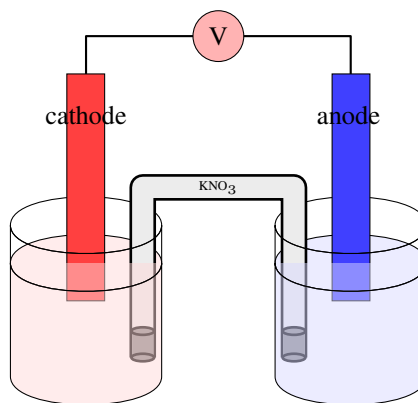
8.2   Standard reduction potentials

In a galvanic cell, each electrode–also called half-cell–has a given potential. When combining two electrodes, we obtain the measurable cell potential. This magnitude represents the force that pushed electrons from the anode to the cathode producing a measurable current. This section covers electrode potentials. We will define the concept of electrode potential, and we will identify the anode and cathode when two electrodes are in contact based on the electrode potentials.

Electrode potentials A galvanic cell consists of two electrodes, an anode, and a cathode. Each electrode contains two chemical species with different redox numbers in contact through an interface. For example, we can build up an electrode by soaking a piece of metallic copper on a solution of copper(II) sulfate. The interface consist of the liquid phase containing $Cu^{2+}_{(aq)}$ in contact with the metal phase made of $Cu_{(s)}$. Each electrode has a reduction potential–$\mathcal{E}$, expressed in volts (V)–that informs about the drive of the redox process in the electrode. The larger this value the stronger the tendency of the redox process to occur.

Standard conditions for reduction potentials The potential of a sin-

gle electrode cannot be accurately measured as electrodes only exist in the context of a two-electrode galvanic cell. Single electrode potentials are defined in a galvanic cell made of the electrode and a reference electrode with null potential under certain conditions. The standard hydrogen electrode (SHE) is universally accepted as the reference electrode in electrochemistry, hence having null potential. The hydrogen electrode contains gas hydrogen in contact with an acidic 1M HCl solution at 25°C with a wire made of platinum–an inert metal–that mediates the electron transfer. Below you can find the reaction involved in the hydrogen electrode:

$$H_2(1 \text{ atm}) \longrightarrow 2\,H_{(aq)}^+(1 \text{ M}) + 2\,e^- \qquad\qquad \mathcal{E}° = 0$$

The voltage of a galvanic cell made of an electrode combined with the reference hydrogen electrode will directly measure the electrode potential. Still, electrode potentials depend on concentration (or pressure for gases) and temperature conditions. The standard conditions for electrode potentials are a molar concentration of 1M for all electrolytes and pressure of 1atm. The electrode potential measured at these conditions is called standard potential $\mathcal{E}°$, where the symbol $°$ represents standard state. At the same time, every redox reaction can be written as a reduction–consuming electrons–or an oxidation reaction–producing electrons. As we tabulate standard electrode potentials, all reactions will be written as reduction reactions and the standard potentials are called standard reduction potential $\mathcal{E}°$.
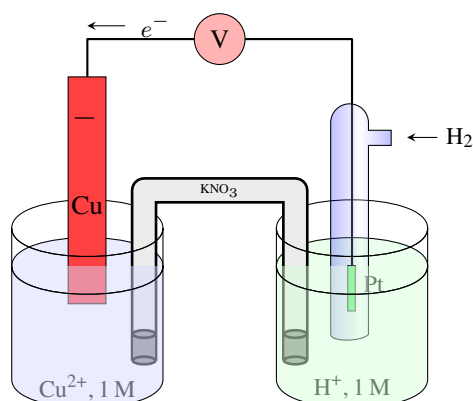

Figure 8.2 A galvanic cell with a hydrogen anode and a copper cathode. The hydrogen electrode is the reference electrode with null electrodic voltage. Hence the voltage of this cell will directly give the copper electrode voltage.

Anodes and cathodes The standard reduction potential of an electrode predicts the tendency of an electrod to act as an anode or cathode. Imagine we have two different electrodes involving the following reaction with the standard potentials indicated on the side, and we need to set up a galvanic cell:

$$Cu_{(aq)}^{2+} + 2\,e^- \longrightarrow Cu_{(s)} \qquad\qquad \mathcal{E}° = +0.34\text{V}$$
$$Zn_{(aq)}^{2+} + 2\,e^- \longrightarrow Zn_{(s)} \qquad\qquad \mathcal{E}° = -0.76\text{V}$$

How to determine which electrode will act as anode and which will act as cathode? The rule is the smaller the electrode potential the more tendency of the electrode to act as an anode. If we compare the copper and zinc electrodes, as the electrode potential of zinc is smaller–more negative–than the electrode potential of copper. Therefore, zinc will

act as an anode and copper will act as a cathode. The standard reduction potential is not affected by the stoichiometry of the reaction. For example, the standard reduction potential of cesium is $-3.03V$:

$$Cs^+ + e^- \rightleftharpoons Cs_{(s)} \qquad\qquad \mathcal{E}° = -3.03V$$

At the same time, the standard reduction potential of two moles of cesium is still $-3.03V$.

$$2\,Cs^+ + 2\,e^- \rightleftharpoons 2\,Cs_{(s)} \qquad\qquad \mathcal{E}° = -3.03V$$

Differently, inverting the reduction reaction switches the sign of the reduction potential. For example, the standard reduction potential of Titanium(II) is $-1.63V$
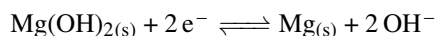
$$Ti^{2+} + 2\,e^- \rightleftharpoons Ti_{(s)} \qquad\qquad \mathcal{E}° = -1.63V$$

while the standard potential of oxidation of Titanium into Titanium(II) is $+1.63V$

$$Ti_{(s)} \rightleftharpoons Ti^{2+} + 2\,e^- \qquad\qquad \mathcal{E}° = +1.63V$$
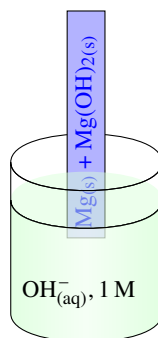

Sample Problem 2

Sketch a semi-cell for the semi reaction below, indicate if the electrode is a solid-liquid electrode or gas-liquid electrode. Assume standard conditions:

$$Mg(OH)_{2(s)} + 2\,e^- \rightleftharpoons Mg_{(s)} + 2\,OH^-$$

SOLUTION

This is a solid-liquid electrode. The solid piece would be made of Magnesium covered with magnesium hydroxide. The liquid phase would contain a base (OH^-). At standard conditions all molarities would be 1M.

◈ STUDY CHECK

Sketch a semi-cell for the semi reaction below, indicate if the electrode is a solid-liquid electrode or gas-liquid electrode. Assume standard conditions:

$$2\,H_2O_{(l)} + 2\,e^- \rightleftharpoons H_{2(g)} + 2\,OH^-_{(aq)}$$
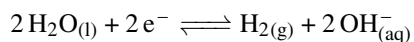
Table 8.1 Standard reduction potentials at 298K

Element	Reaction	$\mathcal{E}°$ (V)	Element	Reaction	$\mathcal{E}°$ (V)
Sr	$Sr^+ + e^- \rightleftharpoons Sr_{(s)}$	-4.10	H	$2H^+ + 2e^- \rightleftharpoons H_{2(g)}$	0.00
Ca	$Ca^+ + e^- \rightleftharpoons Ca_{(s)}$	-3.80	Ag	$AgBr_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Br^-$	+0.07
Li	$Li^+ + e^- \rightleftharpoons Li_{(s)}$	-3.04	S	$S_4O_2^{6-} + 2e^- \rightleftharpoons 2S_2O_2 - 3$	+0.08
Cs	$Cs^+ + e^- \rightleftharpoons Cs_{(s)}$	-3.03	N	$N_{2(g)} + 2H_2O + 6H^+ + 6e^- \rightleftharpoons 2NH_4OH_{(aq)}$	+0.09
Ca	$Ca(OH)_2 + 2e^- \rightleftharpoons Ca_{(s)} + 2OH^-$	-3.02	Hg	$HgO_{(s)} + H_2O + 2e^- \rightleftharpoons Hg(l) + 2OH^-$	+0.10
Ba	$Ba(OH)_2 + 2e^- \rightleftharpoons Ba_{(s)} + 2OH^-$	-2.99	C	$C_{(s)} + 4H^+ + 4e^- \rightleftharpoons CH_{4(g)}$	+0.13
Rb	$Rb^+ + e^- \rightleftharpoons Rb_{(s)}$	-2.98	Sn	$Sn^{4+} + 2e^- \rightleftharpoons Sn_2^+$	+0.15
K	$K^+ + e^- \rightleftharpoons K_{(s)}$	-2.93	Cu	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.159
Ba	$Ba^{2+} + 2e^- \rightleftharpoons Ba_{(s)}$	-2.91	Fe	$3Fe_2O_{3(s)} + 2H^+ + 2e^- \rightleftharpoons 2Fe_3O_{4(s)} + H_2O$	+0.22
Sr	$Sr^{2+} + 2e^- \rightleftharpoons Sr_{(s)}$	-2.90	Ag	$AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^-$	+0.22
Sr	$Sr(OH)_2 + 2e^- \rightleftharpoons Sr_{(s)} + 2OH^-$	-2.88	Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca_{(s)}$	-2.87	Fe	$Fe^+ + e^- \rightleftharpoons Fe_{(s)}$	+0.40
Li	$Li^+ + C_{6(s)} + e^- \rightleftharpoons LiC_{6(s)}$	-2.84	O	$O_{2(g)} + 2H_2O + 4e^- \rightleftharpoons 4OH-_{(aq)}$	+0.40
Na	$Na^+ + e^- \rightleftharpoons Na_{(s)}$	-2.71	Cu	$Cu^+ + e^- \rightleftharpoons Cu_{(s)}$	+0.520
Mg	$Mg(OH)_2 + 2e^- \rightleftharpoons Mg_{(s)} + 2OH^-$	-2.69	C	$CO_{(g)} + 2H^+ + 2e^- \rightleftharpoons C_{(s)} + H_2O$	+0.52
Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg_{(s)}$	-2.37	I	$I_{2(s)} + 2e^- \rightleftharpoons 2I^-$	+0.54
H	$H_{2(g)} + 2e^- \rightleftharpoons 2H^-$	-2.23	Mn	$MnO_4^- + 2H_2O + 3e^- \rightleftharpoons MnO_{2(s)} + 4OH^-$	+0.595
Sr	$Sr^{2+} + 2e^- \rightleftharpoons Sr(Hg)$	-1.79	O	$O_{2(g)} + 2H^+ + 2e^- \rightleftharpoons H_2O_{2(aq)}$	+0.70
Al	$Al^{3+} + 3e^- \rightleftharpoons Al_{(s)}$	-1.66	Fe	$Fe_2O_{3(s)} + 6H^+ + 2e^- \rightleftharpoons 2Fe^{2+} + 3H_2O$	+0.728
Ti	$Ti^{2+} + 2e^- \rightleftharpoons Ti_{(s)}$	-1.63	Fe	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
Ti	$Ti^{3+} + 3e^- \rightleftharpoons Ti_{(s)}$	-1.37	Ag	$Ag^+ + e^- \rightleftharpoons Ag_{(s)}$	+0.80
Ti	$TiO_{(s)} + 2H^+ + 2e^- \rightleftharpoons Ti_{(s)} + H_2O$	-1.31	Hg	$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$	+0.80
Mn	$Mn^{2+} + 2e^- \rightleftharpoons Mn_{(s)}$	-1.18	N	$NO_3^-{}_{(aq)} + 2H^+ + e^- \rightleftharpoons NO_{2(g)} + H_2O$	+0.80
V	$V^{2+} + 2e^- \rightleftharpoons V_{(s)}$	-1.13	Fe	$2FeO_2^{2-} + 5H_2O + 6e^- \rightleftharpoons Fe_2O_{3(s)} + 10OH^-$	+0.81
Ti	$TiO^{2+} + 2H^+ + 4e^- \rightleftharpoons Ti_{(s)} + H_2O$	-0.93	Hg	$Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$	+0.85
Si	$SiO_{2(s)} + 4H^+ + 4e^- \rightleftharpoons Si_{(s)} + 2H_2O$	-0.91	Mn	$MnO_4^- + H^+ + e^- \rightleftharpoons HMnO_4^-$	+0.90
Fe	$Fe_2O_{3(s)} + 3H_2O + 2e^- \rightleftharpoons 2Fe(OH)_{2(s)} + 2OH^-$	-0.86	Hg	$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+0.91
H	$2H_2O + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-$	-0.828	Pd	$Pd^{2+} + 2e^- \rightleftharpoons Pd_{(s)}$	+0.915
Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn_{(s)}$	-0.762	N	$NO_3^-{}_{(aq)} + 4H^+ + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O(l)$	+0.96
Cr	$Cr^{3+} + 3e^- \rightleftharpoons Cr_{(s)}$	-0.74	Fe	$Fe_3O_{4(s)} + 8H^+ + 2e^- \rightleftharpoons 3Fe^{2+} + 4H_2O$	+0.98
Ni	$Ni(OH)_{2(s)} + 2e^- \rightleftharpoons Ni_{(s)} + 2OH^-$	-0.72	Br	$Br_{2(aq)} + 2e^- \rightleftharpoons 2Br^-$	+1.09
Ag	$Ag_2S_{(s)} + 2e^- \rightleftharpoons 2Ag_{(s)} + S2-_{(aq)}$	-0.69	Ag	$Ag_2O_{(s)} + 2H^+ + 2e^- \rightleftharpoons 2Ag_{(s)} + H_2O$	+1.17
Pb	$PbO_{(s)} + H_2O + 2e^- \rightleftharpoons Pb_{(s)} + 2OH^-$	-0.58	Pt	$Pt^{2+} + 2e^- \rightleftharpoons Pt_{(s)}$	+1.188
Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe_{(s)}$	-0.44	Cl	$ClO-4 + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.20
Cr	$Cr^{3+} + e^- \rightleftharpoons Cr_2^+$	-0.42	O	$O_{2(g)} + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
Cd	$Cd^{2+} + 2e^- \rightleftharpoons Cd_{(s)}$	-0.40	Cl	$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-$	+1.36
Cu	$Cu_2O_{(s)} + H_2O + 2e^- \rightleftharpoons 2Cu_{(s)} + 2OH^-$	-0.36	Br	$BrO_3^- + 5H^+ + 4e^- \rightleftharpoons HBrO_{(aq)} + 2H_2O$	+1.45
Pb	$PbSO_{4(s)} + 2e^- \rightleftharpoons Pb_{(s)} + SO_2-4$	-0.36	Br	$2BrO^{3-} + 12H^+ + 10e^- \rightleftharpoons Br_2(l) + 6H_2O$	+1.48
Pb	$PbSO_{4(s)} + 2e^- \rightleftharpoons Pb(Hg) + SO_2-4$	-0.35	Cl	$2ClO^{3-} + 12H^+ + 10e^- \rightleftharpoons Cl_{2(g)} + 6H_2O$	+1.49
Co	$Co^{2+} + 2e^- \rightleftharpoons Co_{(s)}$	-0.28	Mn	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn_2^+ + 4H_2O$	+1.51
Ni	$Ni^{2+} + 2e^- \rightleftharpoons Ni_{(s)}$	-0.25	Au	$Au^{3+} + 3e^- \rightleftharpoons Au_{(s)}$	+1.52
As	$As_{(s)} + 3H^+ + 3e^- \rightleftharpoons AsH_{3(g)}$	-0.23	Pb	$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.69
Ag	$AgI_{(s)} + e^- \rightleftharpoons Ag_{(s)} + I^-$	-0.15	Mn	$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_{2(s)} + 2H_2O$	+1.70
Sn	$Sn^{2+} + 2e^- \rightleftharpoons Sn_{(s)}$	-0.13	Ag	$AgO_{(s)} + 2H^+ + e^- \rightleftharpoons Ag^+ + H_2O$	+1.77
Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb_{(s)}$	-0.126	O	$H_2O_{2(aq)} + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.78
C	$CO_{2(g)} + 2H^+ + 2e^- \rightleftharpoons HCOOH_{(aq)}$	-0.11	Au	$Au^+ + e^- \rightleftharpoons Au_{(s)}$	+1.83
C	$CO_{2(g)} + 2H^+ + 2e^- \rightleftharpoons CO_{(g)} + H_2O$	-0.11	Ag	$Ag^{2+} + e^- \rightleftharpoons Ag^+$	+1.98
Fe	$Fe_3O_{4(s)} + 8H^+ + 8e^- \rightleftharpoons 3Fe_{(s)} + 4H_2O$	-0.08	Mn	$HMnO_4^- + 3H^+ + 2e^- \rightleftharpoons MnO_{2(s)} + 2H_2O$	+2.09
Fe	$Fe^{3+} + 3e^- \rightleftharpoons Fe_{(s)}$	-0.04	Fe	$FeO_2^{4-} + 8H^+ + 3e^- \rightleftharpoons Fe^{3+} + 4H_2O$	+2.20
H	$2H^+ + 2e^- \rightleftharpoons H_{2(g)}$	0.00	F	$F_{2(g)} + 2H^+ + 2e^- \rightleftharpoons 2HF_{(aq)}$	+3.05

Increasing oxidizing strength (decreasing reducing strength)

8.3 Redox reactions in galvanic cells

Galvanic cells consist of an anode and a cathode. The anode carries the oxidation reaction hence producing electrons. The cathode carries the reduction reaction hence consuming electrons. Overall, the number of electrons produced by the anode compensated for the number of electrons consumed by the cathode. so that electrons do not accumulate in the cell. When obtaining the overall redox reaction from two reduction reactions we need to operate in order to take into account the oxidation carried in the anode and the conservation

of charge.

Identifying the anodic and cathodic reaction Let us assume we need to build up a galvanic cell based on the following reactions:

$$V^{2+}_{(aq)} + 2\,e^- \rightleftharpoons V_{(s)} \qquad\qquad \mathcal{E}^\circ = -1.13V$$
$$Au^{3+}_{(aq)} + 3\,e^- \rightleftharpoons Au_{(s)} \qquad\qquad \mathcal{E}^\circ = +1.52V$$

We want to identify the anodic and the cathodic reaction. To do this we should compare the magnitude of the standard reduction potentials for both reactions, the larger this value the larger the tendency of the reaction to proceed as a reduction, and hence the larger the tendency of the electrode based on that reaction to act as a cathode. We have that the reduction of vanadium has a standard reduction potential of -1.13V, whereas the standard reduction potential for the reduction of gold is +1.52V. An electrode made of a piece of vanadium in contact with a solution of vanadium(II) would be the anode and an electrode made of a piece of gold in contact with a solution of gold(III) would be the cathode. Now we can label the reactions as anode and cathode:

$$V^{2+}_{(aq)} + 2\,e^- \rightleftharpoons V_{(s)} \qquad\qquad \mathcal{E}^\circ_{anode} = -1.13V$$
$$Au^{3+}_{(aq)} + 3\,e^- \rightleftharpoons Au_{(s)} \qquad\qquad \mathcal{E}^\circ_{cathode} = +1.52V$$

Below is a representation of the gold-vanadium galvanic cell. The anode made made of vanadium contains metallic vanadium in contact with a solution of vanadium(II), whereas the cathode made made of gold contains metallic gold in contact with a solution of gold(III).
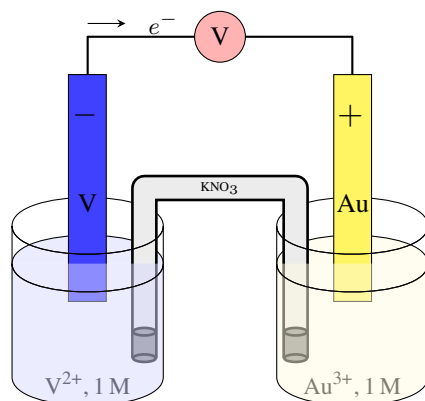
Figure 8.3 A Au-V galvanic cell

Cell potential from electrodic voltages The cell voltage is a combination of the anodic voltage and the cathodic voltage. In particular, the cathodic voltage with respect to the anodic voltage. In the example below we have:

$$3\,V_{(s)} + 2\,Au^{3+}_{(aq)} + 6\,e^- \rightleftharpoons 3\,V^{2+}_{(aq)} + 2\,Au_{(s)} + 6\,e^- \qquad -\mathcal{E}^\circ_{anode} = 1.13 + 1.52 = 2.65V$$
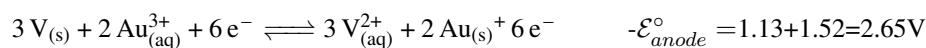
The following equation is used to calculate the cell voltage from the separate electronic potentials:

$$\boxed{\mathcal{E}^\circ_{cell} = \mathcal{E}^\circ_{cathode} - \mathcal{E}^\circ_{anode}} \qquad\qquad (8.1)$$

Electrons flowing The number of electrons flowing in a galvanic cell–specifically the moles of electrons flowing–deppends on the electrons produced in the anode and consumed in the cathode. Given that the overall charge of the cell needs to be conserved:

$$3\,V_{(s)} + 2\,Au^{3+}_{(aq)} + \cancel{6\,e^-} \rightleftharpoons 3\,V^{2+}_{(aq)} + 2\,Au_{(s)}{}^+ \cancel{6\,e^-}$$
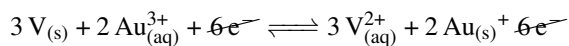
In the example above, for the gold-vanadium galvanic cell, we have that gold consumes three moles of electrons and vanadium produces two moles of electrons, overall six moles of electrons flow through the cell.

Sample Problem 3

We want to build up a galvanic cell based on the reactions below.

$$NO_3{}^-{}_{(aq)} + 4\,H^+ + 3\,e^- \rightleftharpoons NO_{(g)} + 2\,H_2O\,(l) \qquad \mathcal{E}^\circ = +0.96V$$
$$Fe_3O_{4(s)} + 8\,H^+ + 8\,e^- \rightleftharpoons 3\,Fe_{(s)} + 4\,H_2O \qquad \mathcal{E}^\circ = -0.08V$$

Indicate: (a) the anodic and cathodic reactions (b) the balanced overall redox (c) the number of electrons flowing (d) the overall voltage of the cell (e) draw a diagram of the cell

SOLUTION

We have two electronic reactions. The first one results from the reduction of nitrate into nitrogen monoxide, with a standard reduction voltage of 0.96V. The second one results from the reduction of iron(III) oxide into metallic iron, with a standard reduction voltage of -0.08V. The reduction of nitrate would act as cathode–with higher voltage–whereas the oxidation of nitrogen monoxide would act as anode, with lower voltage.
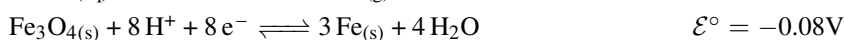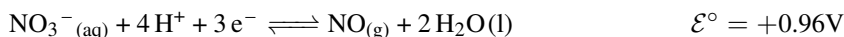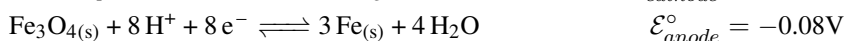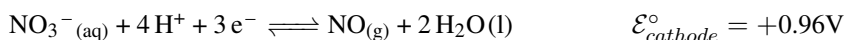
$$NO_3{}^-{}_{(aq)} + 4\,H^+ + 3\,e^- \rightleftharpoons NO_{(g)} + 2\,H_2O\,(l) \qquad \mathcal{E}^\circ_{cathode} = +0.96V$$
$$Fe_3O_{4(s)} + 8\,H^+ + 8\,e^- \rightleftharpoons 3\,Fe_{(s)} + 4\,H_2O \qquad \mathcal{E}^\circ_{anode} = -0.08V$$

To balance the overall redox reaction we need to first invert the anodic reaction,

$$NO_3{}^-{}_{(aq)} + 4\,H^+ + 3\,e^- \rightleftharpoons NO_{(g)} + 2\,H_2O\,(l) \qquad \mathcal{E}^\circ_{cathode} = +0.96V$$
$$3\,Fe_{(s)} + 4\,H_2O \rightleftharpoons Fe_3O_{4(s)} + 8\,H^+ + 8\,e^- \qquad \text{-}\mathcal{E}^\circ_{anode} = +0.08V$$

then to multiply the first reaction by eight and the second reaction by three without altering the electronic voltages:

$$8\,NO_3{}^-{}_{(aq)} + 23\,H^+ + 24\,e^- \rightleftharpoons 8\,NO_{(g)} + 16\,H_2O\,(l) \qquad \mathcal{E}^\circ_{cathode} = +0.96V$$
$$9\,Fe_{(s)} + 12\,H_2O \rightleftharpoons 3\,Fe_3O_{4(s)} + 24\,H^+ + 24\,e^- \qquad \text{-}\mathcal{E}^\circ_{anode} = +0.08V$$

Now we can add both reaction:

$$8\,NO_3{}^-{}_{(aq)} + 23\,H^+ + 24\,e^- \rightleftharpoons 8\,NO_{(g)} + 16\,H_2O\,(l) \qquad \mathcal{E}^\circ_{cathode} = +0.96V$$
$$9\,Fe_{(s)} + 12\,H_2O \rightleftharpoons 3\,Fe_3O_{4(s)} + 24\,H^+ + 24\,e^- \qquad \text{-}\mathcal{E}^\circ_{anode} = +0.08V$$

$$8\,NO_3{}^-{}_{(aq)} + 23\,H^+ + 9\,Fe_{(s)} + 12\,H_2O + 24\,e^- \rightleftharpoons 8\,NO_{(g)} +$$

$$+ 16\,H_2O\,(l) + 3\,Fe_3O_{4(s)} + 24\,H^+ + 24\,e^- \qquad \mathcal{E}^\circ_{cell}$$
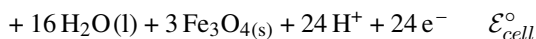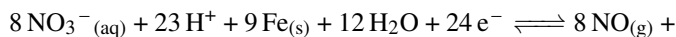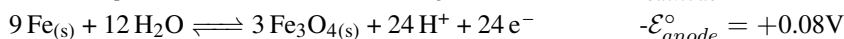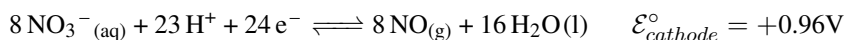
We would have to remove water molecules as they appear in both sides and protons as well: $8\,NO_3{}^-{}_{(aq)} + {} + 9\,Fe_{(s)} + {} + \cancel{24\,e^-} \rightleftharpoons 8\,NO_{(g)} +$

$$+ 4\,H_2O_{(l)} + 3\,Fe_3O_{4(s)} + H_{(aq)}{}^+ + \cancel{24\,e^-} \qquad \mathcal{E}^\circ_{cell}$$
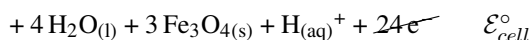
Overall there is 24 moles of electrons going through the cell. The overall voltage would be:

$$\mathcal{E}^\circ_{cell} = \mathcal{E}^\circ_{cathode} - \mathcal{E}^\circ_{anode} = (0.96) - (-0.08) = 1.04V$$

The diagram of the cell is presented below:
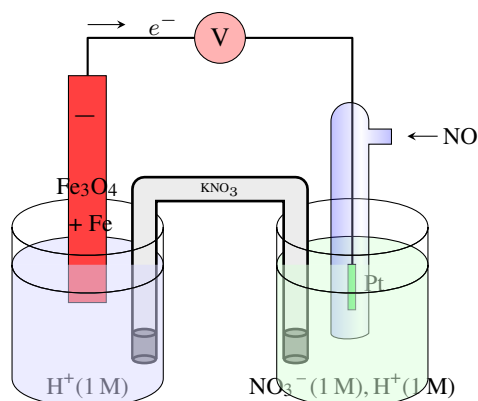
◈ **STUDY CHECK**

We want to build up a galvanic cell based on the reactions below.

$$Cr^{3+} + e^- \rightleftharpoons Cr^{2+} \qquad\qquad \mathcal{E}° = -0.42V$$
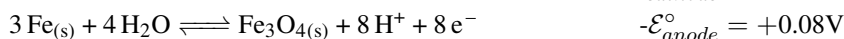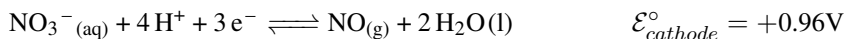$$Cu^+ + e^- \rightleftharpoons Cu_{(s)} \qquad\qquad \mathcal{E}° = 0.52V$$

Indicate: (a) the anodic and cathodic reactions (b) the balanced overall redox (c) the number of electrons flowing (d) the overall voltage of the cell
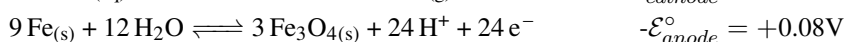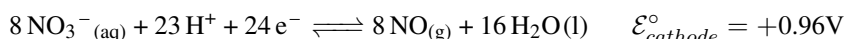
8.4 Line notation for galvanic cells

There is a quick and easy way to represent a galvanic cell without having to draw the whole cell diagram. This is called the line notation and galvanic cells are represented in a single line, starting from left to right. The anode is presented in the left, starting from the metallic part and followed by the electrolyte. A single line represents the liquid-solid contact. A double line represents the salt bridge and the cathode is represented in the right, starting for the electrolyte and finishing by the metal. As you can see, the line notation respect all interphase present in the cells: from left to right we have solid, liquid in contact with the salt bridge which is in contact with the liquid part of the cathode and finally we have the solid part of the cathode. For example, the line notation of Daniell cell is:

$$Zn \,|\, Zn^{2+}(1\ M) \,\|\, Cu^{2+}(1\ M) \,|\, Cu$$
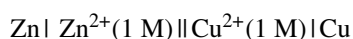
In case there are several electrolytes in any of the electrodes, as all species are in liquid phase we separate them with just a comma. For example, in the galvanic cell below the cathode contains two different states of iron and uses Pt for the charge transfer:

$$Zn \,|\, Zn^{2+}(1\ M) \,\|\, Fe^{2+}, Fe^{3+}(1\ M) \,|\, Pt$$

Gases should also be included in the notation with their corresponding pressure. For example, the hydrogen electrode would be written as:

$$Pt \,|\, H_2(1\ atm) \,|\, H^+(1\ M) \,|$$
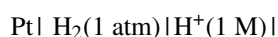
Sample Problem 4

Give the line notation for the galvanic cell below:
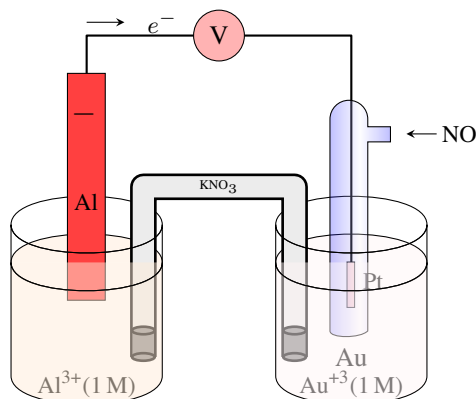
SOLUTION

We have that the anode is based on aluminum whereas the cathode is based on gold.
We have two metallic electrodes. The line notations of the galvanic cell will be:

$$Al \,|\, Al^{3+}(1\,M) \,\|\, Au^{3+}(1\,M) \,|\, Au$$

◆ STUDY CHECK

Give the line notation for the galvanic cell below:
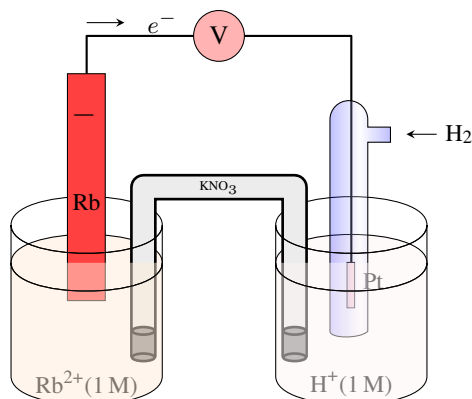
8.5 Cell potential, Gibbs free energy, and equilibrium constant

Cell potentials are electrochemistry functions that inform about the voltage generated by a galvanic cell. Gibbs free energies are thermodynamic functions that inform about the maximum work–in particular non-expansion- work–that one can extract from a system, under constant pressure and temperature. Both properties are related. At the same time, the equilibrium constant of a system is related to the Gibbs free energy change. Hence, these three properties are indeed related: the cell potential, the Gibbs free energy, and the equilibrium constant.

Maximum work given by a galvanic cell Galvanic cells produce electricity and hence they generate work. The maximum work produced by a galvanic cell is

given by:

$$w_{max} = -n_e \cdot F \cdot \mathcal{E}_{cell} \tag{8.2}$$

where:

> n_e is the number of moles of electrons flowing through the cell
>
> F is Faraday's constant (9.6485×10^4 C/mol), a constant used to convert from moles of electrons to coulombs (a charge unit)
>
> w_{max} is the maximum work produced by the cell (in J)
>
> $\mathcal{E}_{cell}$ is the cell voltage (in V)

For example, a galvanic cell that produced 3V with a flow of 4 electrons can generate less than

$$w_{max} = -n_e \cdot F \cdot \mathcal{E}_{cell} = -4 \cdot 9.6485 \times 10^4 \cdot 3 = -1157820J = -116KJ$$

The negative sign on the formula indicates that work is being produced (and not consumed).

Reduction potentials and Gibbs free energy The cell potential of a galvanic cell represents the voltage experienced by the electrons flowing through the cell. The voltage or potential difference–volts are the SI units–is a force that drives the electric flow. In other words, the potential difference generated by a galvanic cell tells about the work needed to carry an electric charge in the cell. A Volt is defined as one joule (J) per coulomb (C) of charge. The maximum amount of work that an electron can do in a galvanic cell is given by the potential difference of the cell times the charge. At the same time, in chemistry, the maximum–nonexpansive–work that a system can do, in reversible conditions, is given by the Gibbs free energy. As both the cell voltage and Gibbs free energy are related to the work generated in the cell, it is simple to see how both thermodynamic functions are related:

$$\Delta G^\circ = -n_e \cdot F \cdot \mathcal{E}_{cell}^\circ \tag{8.3}$$

where:

> n_e is the number of moles of electrons flowing through the cell
>
> F is Faraday's constant (9.6485×10^4 C/mol), a constant used to convert from moles of electrons to coulombs (a charge unit)
>
> ΔG° is the standard Gibbs free energy change (in J)
>
> $\mathcal{E}_{cell}^\circ$ is the standard cell voltage (in V)

For example, for the redox reaction happening in a galvanic cell:

$$3\,V_{(s)} + 2\,Au^{3+}_{(aq)} + 6\,e^- \rightleftharpoons 3\,V^{2+}_{(aq)} + 2\,Au_{(s)} + 6\,e^- \qquad \mathcal{E}_{cell}^\circ = 2.65V$$
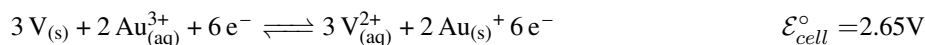
we have that the cell voltage if 2.65V. As there are six moles of electron flowing through the cell, we have that the change in Gibbs free energy in this reaction would be:

$$\Delta G^\circ = -n_e \cdot F \cdot \mathcal{E}_{cell}^\circ = -6 \cdot 9.6485 \times 10^4 \cdot 2.65 = -1534111.5J = -1534KJ$$

The negative sign in the Formula 8.3 is critical. As cell voltages can only be positive numbers, Gibbs free energy changes for working–spontaneously–galvanic cells will always be negative. At the same time, Formula 8.3 gives the maximum work produced by a galvanic cell working at reversible conditions. In other words, real working cells that produce electricity will always produce voltage lower than the one given by Formula 8.3, as these do not function reversibly. Finally, there exist an equivalent formula to Formula 8.3 without the standard sign for conditions different than the standard ones.

> **Sample Problem 5**
>
> Calculate the standard Gibbs free energy change ΔG° for the following redox reaction:
>
> $$2\,Au^+ + Ni_{(s)} \rightleftharpoons 2\,Au_{(s)} + Ni^{2+} \qquad\qquad \mathcal{E}^\circ_{cell} = 2.08V$$
>
> **SOLUTION**
>
> We have that in the reaction there is a flow of two moles of electrons. As we know the standard cell potential, we can easily calculate the value of ΔG°:
>
> $$-n_e \cdot F \cdot \mathcal{E}^\circ_{cell} = 2 \cdot 9.6485 \times 10^4 \cdot 2.08 = -401377J = -401.4KJ$$
>
> As the cell voltage is a positive property, ΔG° should be negative. This means that the cell will produce electricity spontaneously.
>
> ◈ **STUDY CHECK**
>
> Calculate the standard Gibbs free energy change ΔG° for the following redox reaction:
>
> $$F_{2(g)} + 2\,H^+ + 2\,e^- + 2\,Cs_{(s)} \rightleftharpoons 2\,HF_{(aq)} + 2\,Cs^+ + 2\,e^- \qquad \mathcal{E}^\circ_{cell} = 6.08V$$
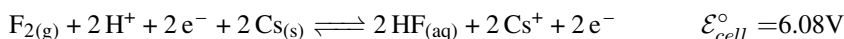
Reduction potentials and equilibrium constant One of the uses of standard reduction potentials ($\mathcal{E}^\circ$) is to compute standard Gibbs free energy changes from galvanic cell potentials. Another use is to calculate the equilibrium constant (K) from electrochemical data. As standard reduction potentials are related to standard Gibbs free energies and ΔG° is related to the equilibrium constant, we can conclude that $\mathcal{E}^\circ$ is related to K. We use the following equation to compute equilibrium constants from electrochemical data:

$$\boxed{\ln K = \frac{n_e \cdot F \cdot \mathcal{E}^\circ_{cell}}{RT}} \qquad\qquad (8.4)$$

where:

K is the equilibrium constant

n_e is the number of electrons (a pure number) flowing through the cell

F is Faraday's constant (9.6485×10^4C/mol)

$\mathcal{E}^\circ_{cell}$ is the standard cell voltage (in V)

R is the constant of the gases in energy units (8.314J/molK)

T is the absolute temperature (kelvins)

For example, the reduction of zinc(II) to give metallic zinc is given by:

$$Zn^{2+}_{(aq)} + 2\,e^- \longrightarrow Zn_{(s)} \qquad\qquad \mathcal{E}^\circ = -0.76V$$

We can obtain the standard equilibrium constant at 298K by doing:

$$\ln K = \frac{n_e \cdot F \cdot \mathcal{E}^\circ_{cell}}{RT} = \frac{2 \cdot 96485 \cdot (-0.76)}{8.314 \cdot 298} = -59.19$$

Hence the value of the equilibrium constant at 298K would be 1.96×10^{26}. As K is smaller than one, this means that at 298K ionic zinc will not undergo the reduction process spontaneously, and there are more reactants than products in equilibrium.

8.6 Electrochemical series: dissolving metals in acid

Metals dissolve forming ions. The dissolution of a metal involves a redox reaction in which a metallic element transforms into its ionic state. During this process, on one hand, the metal loses electrons producing cations and hence the metal is being oxidized. On the other hand, the solvent reduces. Acids contain protons that can reduce to hydrogen. Indeed, one can use acids to dissolve metals like using water to dissolve table salt. However, not all acids will dissolve a given metal. The electrochemical series is a list of redox pairs going from low standard reduction potential to high standard reduction potential. Using this series, we can find out whether a metal will be dissolved by an acid.

Reducing character We can use the standard reduction potentials table to compare the reducing character of two redox pairs. For example, if we compare the pairs Fe/Fe^{2+} and Zn/Zn^{2+}. We have that the reduction potentials are:

$$Fe^{3+} + 3\,e^- \rightleftharpoons Fe_{(s)} \qquad\qquad \mathcal{E}_1^\circ = -0.04\text{V}$$
$$Zn^{2+} + 2\,e^- \rightleftharpoons Zn_{(s)} \qquad\qquad \mathcal{E}_2^\circ = -0.762\text{V}$$

We have that the smaller $\mathcal{E}^\circ$ the stronger the reducing character. Hence, the pair Zn/Zn^{2+} is more reducing than Fe/Fe^{2+}. We can also compare the oxidizing character of two redox pairs. For example, if we compare the pairs O$_2$/H$_2$O and Ag$^+$/Ag. We have that the reduction potentials are:

$$O_{2(g)} + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O \qquad\qquad \mathcal{E}_1^\circ = +1.23\text{V}$$
$$Ag^+ + e^- \rightleftharpoons Ag_{(s)} \qquad\qquad \mathcal{E}_2^\circ = +0.802\text{V}$$

We have that the larger $\mathcal{E}^\circ$ the stronger the oxidizing character. Hence, the pair O$_2$/H$_2$O is more oxidizing than Ag$^+$/Ag.

Sample Problem 6

Compare the reducing power of the following species:

$$Fe^{2+} \text{ and } PbSO_{4(s)}$$

SOLUTION

The larger the standard reduction potential the stronger the reducing power of a redox pair. For Iron(II) we have that the standard reduction potential for the Fe^{2+}/Fe$_{(s)}$ pair is -0.44V. For the PbSO$_{4(s)}$/Pb$_{(s)}$ pair is -0.35V. The PbSO$_{4(s)}$/Pb$_{(s)}$ pair is more reducing.

◆ **STUDY CHECK**

Compare the oxidizing power of the following species:

$$Cu_2O_{(s)} \text{ and } BrO_3{}^-$$
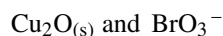
Can an acid dissolve a metal? Let us compare the standard redox potential for two different redox pairs: the reduction of ionic zinc into metallic zinc and the reduction of a proton (found in any acid) into hydrogen

$$Zn^{2+} + 2\,e^- \rightleftharpoons Zn_{(s)} \qquad\qquad \mathcal{E}_1^\circ = -0.762\text{V}$$
$$2\,H^+ + 2\,e^- \rightleftharpoons H_{2(g)} \qquad\qquad \mathcal{E}_2^\circ = +0.00\text{V}$$

The redox potential of zinc is smaller than the potential of protons. In other words, hydrogen has a stronger oxidizing character than zinc, and zinc has a stronger reducing character than hydrogen. This means that hydrogen would oxidize zinc producing Zn^{2+} and reduce itself producing $H_{2(g)}$, and hence when pairing both elements, zinc will likely dissolve in a solution containg an acid, at standard conditons. By comparing a redox pair with the origin of the reduction scale, we can find out whether a metal will dissolve in simple acids (nonoxidizing acidsm e.g. HCl). If the redox potential of the metal is lower than zero then the metal will dissolve in acid. For example, aluminum, lead, or iron will dissolve in HCl. Differently, gold or silver will not. HCl is a nonoxidizing acid. Other acids such as HNO_3 are called oxidizing acids as they have a stronger oxidizing character than hydrochloric acid–a larger redox potential (0.80V). This is because its reduction potential is higher than zero, and as such, they have a stronger capacity to oxidize metals than hydrochloric acid. For example, we can find out whether gold or silver will be dissolved in nitric acid by comparing both redox pairs:

$$Au^+ + e^- \rightleftharpoons Au_{(s)} \qquad\qquad \mathcal{E}_1^\circ = +1.83V$$
$$Ag^+ + e^- \rightleftharpoons Ag_{(s)} \qquad\qquad \mathcal{E}_2^\circ = +0.80V$$
$$NO_3^-{}_{(aq)} + 2\,H^+ + e^- \rightleftharpoons NO_{2(g)} + H_2O \qquad\qquad \mathcal{E}_3^\circ = +0.80V$$
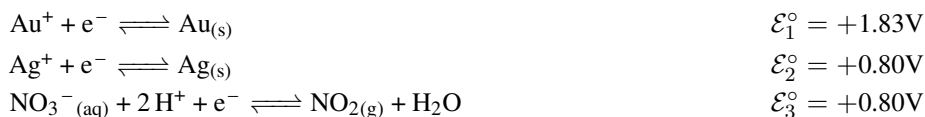
We have that nitric acid will dissolve silver ($\mathcal{E}_2^\circ \simeq \mathcal{E}_3^\circ$) but not gold ($\mathcal{E}_1^\circ > \mathcal{E}_3^\circ$).

8.7 Nernst equation

A galvanic cell connected to a potentiometer works at equilibrium. That means that neither reactants are being consumed nor products are being formed. In working conditions, as a real battery produces electricity reactants are consumed and products are formed. As the galvanic cell works, the concentration of the species inside the cell change and cell potential is certainly affected by that. Standard conditions do not hold anymore as molarities are different than 1M. The Nernst equation–the name honors Walther Nerns, a german electrochemist–gives the dependence of the cell potential with the molarity of the species involved in the redox reaction happening at the cell.

The Nernst equation applied to an electrode The Nernst equation gives the dependence of the cell voltage with the concentration of the ions involved in the redox reaction behind the cell, and with temperature. As such, it is used to compute cell voltage outside the standard conditions. The Nernst equation is given by:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{R \cdot T}{n_e \cdot F} \ln Q \qquad\qquad (8.5)$$

where:

$\mathcal{E}$ is the cell voltage (in V)

$\mathcal{E}^\circ$ is the standard cell voltage (in V)

R is the constant of the gases in energy units (8.314J/molK)

T is the absolute temperature (kelvins)

F is Faraday's constant (9.6485×10^4C/mol)

n_e is the number of electrons in the redox reaction

$Q = \frac{\text{Products}}{\text{Reactants}}$ is the reaction quotient

$\frac{R \cdot T}{F}$ is 0.025693V at 298.15K

For example, for the electrodic reaction representing the oxygen reduction, the standard voltage at standard conditions ($[\text{H}^+]$=1M and p_{O_2} =1atm, mind these are very acidic conditions) is given by:

$$4\,\text{H}^+_{(aq)} + 4\,\text{e}^- + \text{O}_{2(g)} \longrightarrow 2\,\text{H}_2\text{O}_{(l)} \qquad\qquad \mathcal{E}^\circ = +1.23\text{V}$$

However, at $[\text{H}^+]$=10^{-7}M (neutral PH) the electrodic voltage is lower

$$\mathcal{E} = \mathcal{E}^\circ - \frac{R \cdot T}{n_e \cdot F} \ln Q = 1.23 - \frac{8.314 \cdot 298.15}{4 \cdot 96485} \ln \frac{1}{(10^{-7})^4} = 0.81V$$

Hence, it is easier to reduce oxygen at neutral PH than it is at very acidic PH.

$$4\,\text{H}^+_{(aq)} + 4\,\text{e}^- + \text{O}_{2(g)} \longrightarrow 2\,\text{H}_2\text{O}_{(l)} \qquad\qquad \mathcal{E} = +0.81\text{V}$$
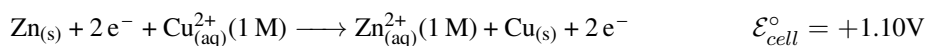
In general, for electrodic reactions involving a single cation, the molarity of this ion will be placed on the bottom of Q. For electrodict reactions involving a single anion, the molarity of this ion will be placed on the top of Q.

The Nernst equation applied to a galvanic cell We can also apply the Nernst's equation to a galvanic cell, for example the Daniell cell:

$$\text{Zn} \,|\, \text{Zn}^{2+}(1\text{ M}) \,\|\, \text{Cu}^{2+}(1\text{ M}) \,|\, \text{Cu}$$
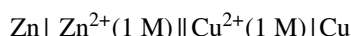
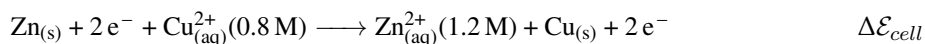The redox reaction behind this cell oxidizes zinc and reduces copper, with a redox standard potential of 1.10V, with all concentrations fixed at 1M:

$$\text{Zn}_{(s)} + 2\,\text{e}^- + \text{Cu}^{2+}_{(aq)}(1\text{ M}) \longrightarrow \text{Zn}^{2+}_{(aq)}(1\text{ M}) + \text{Cu}_{(s)} + 2\,\text{e}^- \qquad \mathcal{E}^\circ_{cell} = +1.10\text{V}$$

For nonstandard conditions we have that as Zinc is being oxidized, its ionic concentration will increase, whereas as Copper is being reduced its concentration will decrease. One can envision the following galvanic cell,

$$\text{Zn} \,|\, \text{Zn}^{2+}(1.2\text{M}) \,\|\, \text{Cu}^{2+}(0.8\text{ M}) \,|\, \text{Cu}$$
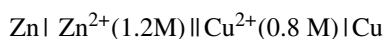
in which the following redox reaction occurs

$$\text{Zn}_{(s)} + 2\,\text{e}^- + \text{Cu}^{2+}_{(aq)}(0.8\text{ M}) \longrightarrow \text{Zn}^{2+}_{(aq)}(1.2\text{ M}) + \text{Cu}_{(s)} + 2\,\text{e}^- \qquad \Delta\mathcal{E}_{cell}$$

Applying Nernst's equation at 298.15K we have:

$$\Delta\mathcal{E}_{cell} = \Delta\mathcal{E}^\circ_{cell} - \frac{R \cdot T}{n_e \cdot F} \ln Q$$

$$\Delta\mathcal{E}_{cell} = 1.10 - \frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{1.2}{0.8} = 1.08V$$

We have that as the galvanic cell is being consumed, the overall cell potential has decreased. For overall redox reactions behind galvanic cells involving a single ionic species in the anode and cathode, the anode molarity will be on the top side of Q whereas the cathode molarity will be on the bottom:

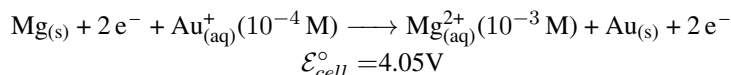$$Q = \frac{\text{anode}}{\text{cathode}}$$

Sample Problem 7

For the galvanic cell below:

$$\text{Mg} \,|\, \text{Mg}^{2+}(10^{-4}\,\text{M}) \,\|\, \text{Au}^+(10^{-3}\,\text{M}) \,|\, \text{Au}$$

(a) Calculate the standard voltage of the cell, given $\mathcal{E}^\circ(\text{Au}^+/\text{Au})=1.69\text{V}$ and $\mathcal{E}^\circ(\text{Mg}^{2+}/\text{Mg})=-2.36\text{V}$ (b) calculate the cell potential at 298.15K **SOLUTION**

The redox reaction being this galvanic cell is indicated below with the standard cell voltage obtained by doing $\mathcal{E}^\circ_{cathode} - \mathcal{E}^\circ_{anode}$:

$$\text{Mg}_{(s)} + 2\,e^- + \text{Au}^+_{(aq)}(10^{-4}\,\text{M}) \longrightarrow \text{Mg}^{2+}_{(aq)}(10^{-3}\,\text{M}) + \text{Au}_{(s)} + 2\,e^-$$
$$\mathcal{E}^\circ_{cell} = 4.05\text{V}$$

We have that two electrons flow though the cell. To calculate the cell potential at 298.15K we apply Nernst equation. While calculating Q we have to place the anodic concentration on top and the cathodic on the bottom:

$$\Delta\mathcal{E}_{cell} = \Delta\mathcal{E}^\circ_{cell} - \frac{R \cdot T}{n_e \cdot F} \ln Q = 4.05 - \frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{10^{-4}}{10^{-3}} = 4.07V$$

◈ **STUDY CHECK**

For the galvanic cell below:

$$\text{Pb} \,|\, \text{Pb}^{2+}(10^{-1}\,\text{M}) \,\|\, \text{Ce}^{4+}, \text{Ce}^{2+}(10^{-2}\,\text{M}) \,|\, \text{Pt}$$

(a) Calculate the standard voltage of the cell, given $\mathcal{E}^\circ(\text{Pb}^{2+}/\text{Pb})=-0.13\text{V}$ and $\mathcal{E}^\circ(\text{Ce}^{4+}/\text{Ce}^{2+})=1.61\text{V}$ (b) Calculate the cell potential at 298.15K

The Nernst equation and a drained galvanic cell A drained galvanic cell loses its capacity to produce voltage. At the same time, when a galvanic cell is drained all ionic concentrations have changed from the initial molarities used to build up the cell. Overall, we have that

$$\boxed{\Delta\mathcal{E} = 0} \qquad \text{drained cell} \qquad (8.6)$$

Concentration cells What caused a voltage difference in a galvanic cell is the differences in reduction potentials of the anode and cathode. By selecting cathodes with larger positive $\mathcal{E}^\circ$ and anodes with large negative $\mathcal{E}^\circ$ we can achieve large cell potentials. At the same time, the Nernst equations tell us that $\mathcal{E}$ depends on molarity, hence we could potentially select the same anode and cathode and use the molarity terms in the Nernt equation to drive the potential difference. This is the principle behind concentration cells. These types of galvanic cells contain the same material in the anode and cathode but with different concentrations. The anode is the less concentrated electrode, whereas the cathode is the most concentrated electrode. The concentration difference is what drives the cell potential. Concentration cells in general produce very low voltages, even with very high concentration differences. For example, for the cell:

$$\text{Zn} \,|\, \text{Zn}^{2+}(10^{-5}\,\text{M}) \,|\, \text{Zn}^{2+}(10^{5}\,\text{M}) \,|\, \text{Zn}$$
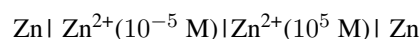
we have that $\mathcal{E}^\circ = +0.29\text{V}$. At the same time, good concentration cells have very low anodic concentrations and very large cathodic concentrations. For concentration cells we have that as both electrodes are made of the same material $\Delta\mathcal{E}^\circ=0$. Hence, Nernst

equation for a concentration cell is simplified to:

$$\Delta\mathcal{E}_{cell} = -\frac{R \cdot T}{n_e \cdot F} \ln Q \quad \text{where } Q = \frac{[\text{anode}]}{[\text{cathode}]}$$
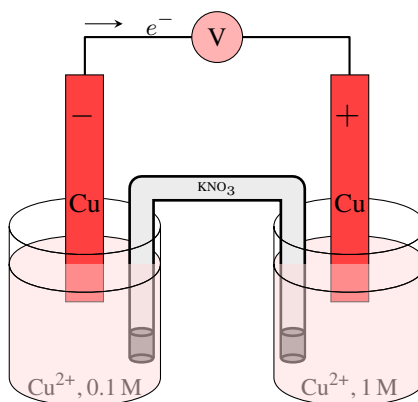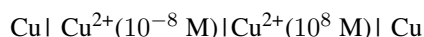

Figure 8.4 A concentration cell

Sample Problem 8

For the concentration cell below:

$$Cu \mid Cu^{2+}(10^{-8} \text{ M}) \mid Cu^{2+}(10^{8} \text{ M}) \mid Cu$$

(a) Identify the anode and the cathode (b) calculate the cell potential at 298.15K

SOLUTION

The electrode potential depends on concentration. The smaller the concentration the lower the cell potential. On the other hand, we have that electrodes with lower cell potential have a stronger tendency to act as anodes, wheres electrodes with higher cell potential have a stronger tendency to act as cathodes. The less concentrated electrode on the left is the anode, whereas the more concentrated electrode on the right is the cathode. To calculate the cell voltage we use Nernst equation at 298.15K and given that two electrons flow though the cell:

$$\Delta\mathcal{E}_{cell} = -\frac{R \cdot T}{n_e \cdot F} \ln Q = -\frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{10^{-8}}{10^{8}} = 0.47V$$

◈ **STUDY CHECK**

For the concentration cell below:

$$Au \mid Au^{3+}(10^{2} \text{ M}) \mid Au^{3+}(10^{-1} \text{ M}) \mid Au$$

(a) Identify the anode and the cathode (b) calculate the cell potential at 298.15K

Ion-selective electrodes Ion-selective electrodes are electrochemical electrodes sensitive to a given ion. One example is the hydrogen electrode, which electrodic voltage varies depending on the PH of the solution in the cell. This principle is used in PH meters, chemical instruments employed to measure the PH of aqueous solutions. A PH meter contains an electrochemical cell–a glass electrode–in which one of the electrodes is sensitive to protons and the other electrode is kept as a reference inside a glass bulb that can be dipped onto solutions. One can use several electrodes as a reference, with fixed molarities. The reference electrode makes contact with the external solution by means of a miniature salt bridge. A common one is the calomel electrode:
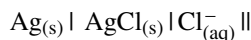
$Hg_2Cl_{2(s)} \,|\, AuCl_{(s)} \,|\, Hg_{(l)} \,\|$ $\hspace{6cm}$ $\mathcal{E}° = 0.27V$

The redox reaction behind this electrode is:

$$H_2Cl_{2(s)} + 2\,e^- + \; \longrightarrow 2\,H^+_{(aq)} + 2\,Hg_{(l)}$$
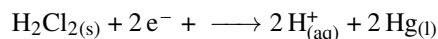
Another common reference electrode is the Ag/AgCl electrode:

$Ag_{(s)} \,|\, AgCl_{(s)} \,|\, Cl^-_{(aq)} \,\|$ $\hspace{6cm}$ $\mathcal{E} = 0.197V$

PH meters need to be calibrated with buffer solutions of a known PH, and their potential varies linearly with PH. There are other ion-sensitive electrodes that can be used to detect a variety of ions such as ammonium, calcium or sodium.
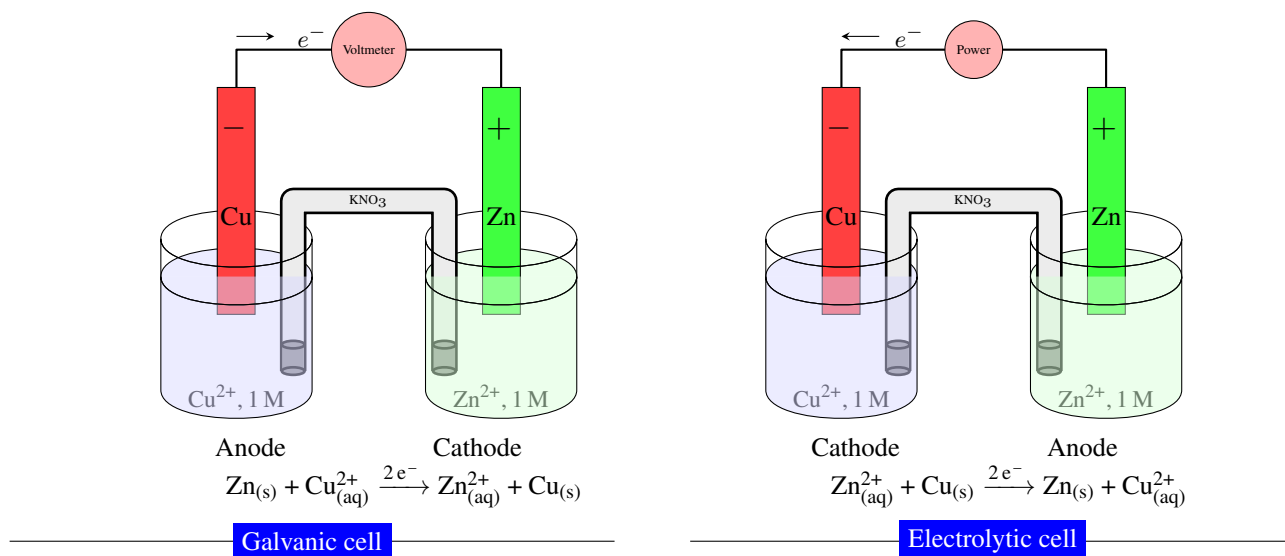

Figure 8.5 A galvanic cell produces voltage from a redox reaction, whereas an electrolytic cell uses voltage to produce a redox reaction. Anodes and cathodes have the opposite sign notation, electrons flow from anode to cathode, whereas ions move towards the electrode of same name (e.g anions migrate towards the anode). However, galvanic anodes are electrolytic cathodes and viceversa.

8.8 Electrolysis

Electrolysis is a process in which an electric current is forced through a chemical system to induce a chemical reaction that otherwise would not happen spontaneously. Galvanic cells and electrolytic cells follow an opposite sign notation, with anodes being labeled with a positive sign and cathodes with a negative sign in electrolytic cells. Furthermore, the galvanic anode becomes the electrolytic cathode, whereas the galvanic cathode becomes the electrolytic anode.

Galvanic cell vs. electrolytic cell A galvanic cell generates voltage through a spontaneous redox reaction. The electrons are produced in the anode and consumed in the cathode. Anions migrate towards the anode and cations towards the cathode. A voltmeter is used to measure the cell voltage. An electrolytic cell uses an externally applied voltage to force a nonspontaneous redox reaction with a negative

voltage. Electrolysis has many applications in science, such as battery charging, metal extraction, production of non-metals, or metal refining. In an electrolytic cell, electrons still flow from the anode to the cathode, and anions also migrate towards the anode, whereas cathodes migrate towards the anode. However, the anode in an electrolytic cell becomes the cathode in the equivalent galvanic cell, whereas the electrolytic cathode becomes the galvanic anode. This is because the externally applied voltage reverts the nature of the electrodes.

Intensity, charge and time The intensity circulating through an electric circuit refers to the charge circulated per unit of time, to the coulombs per second. Rememer that the unit of intensity is the Ampere (A) that equals to coulombs per second (C/s). At the same time, Faraday's constant is used to relate moles of electrons with coulombs, as F is 96485C/mol e^-. We can hence calculate the moles of electrons circulating in a circuit from the intensity and time. For example, an intensity of 10A circulating for 60seconds will correspond to

$$60\,\cancel{s} \times \frac{10\,\cancel{C}}{1\,\cancel{s}} \times \frac{1 \text{ mol } e^-}{96485\,\cancel{C}} = 6.21 \times 10^{-3} \text{moles of } e^-$$

We can also use reaction stoichiometry to relate the moles of electrons flowing in the electrolytic cell with the moles of chemicals produced or consumes. For example, for the redox reaction behind Daniell's cell, we have that in an electrolytic cell, Zinc deposits on the cathode whereas nickel dissolves in the anode. Hence, the cathode will become heavier, whereas the anode will become lighter. We intend to calculate the number of moles of Zinc deposited after applying 10A for 60 seconds. We have that the redox reaction is:

$$Zn^{2+}_{(aq)} + Cu_{(s)} \xrightarrow{2\,e^-} Zn_{(s)} + Cu^{2+}_{(aq)}$$
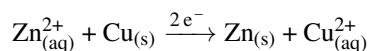
Hence:

$$60\,\cancel{s} \times \frac{10\,\cancel{C}}{1\,\cancel{s}} \times \frac{1 \text{ mol } e^-}{96485\,\cancel{C}} \times \frac{1 \text{ moles of } Zn}{2 \text{ moles of } e^-} = 3.10 \times 10^{-3} \text{moles of } Zn$$

Sample Problem 9

How much time should a 3A current be applied in order to produce 5×10^{-4} moles of Zinc in a Danielle electrolytic cell?

SOLUTION

We will start by using the reaction stoichiometry to convert the moles of Zn produced into moles of electrons flowing through the cell (given that two electrons are involved in the redox reaction), to then convert the moles of electrons into coulombs using Faraday's constant, and the coulombs into ampers:

$$5 \times 10^{-4} \cancel{\text{moles of Zn}} \times \frac{2 \cancel{\text{moles of } e^-}}{1 \cancel{\text{mole of Zn}}} \times \frac{96485 \text{ C}}{1 \cancel{\text{moles of } e^-}} \times \frac{1 \text{ s}}{3 \text{ C}} = 32.16\text{s}$$

♦ **STUDY CHECK**

How much intensity should be applied for 30 seconds to an electrolytic cell based on the reaction below in order to produce 2×10^{-5} moles of Ni.

$$3\,Ni^{2+}_{(aq)} + 2\,Cr_{(s)} \xrightarrow{6\,e^-} 2\,Cr^{3+}_{(aq)} + 3\,Ni_{(s)}$$
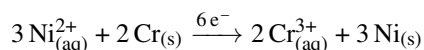
The electrolysis of water Water molecules can be split into gas hydrogen and oxygen. The oxidation of water produces oxygen,

$$H_2O_{(l)} \longrightarrow O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^- \qquad\qquad -\mathcal{E}°\text{=-1.23}$$

and the reduction of water produces hydrogen,

$$4\,H_2O_{(l)} + 4\,e^- \longrightarrow 2\,H_{2(g)} + 4\,OH^-_{(aq)} \qquad\qquad \mathcal{E}°\text{=-0.83}$$
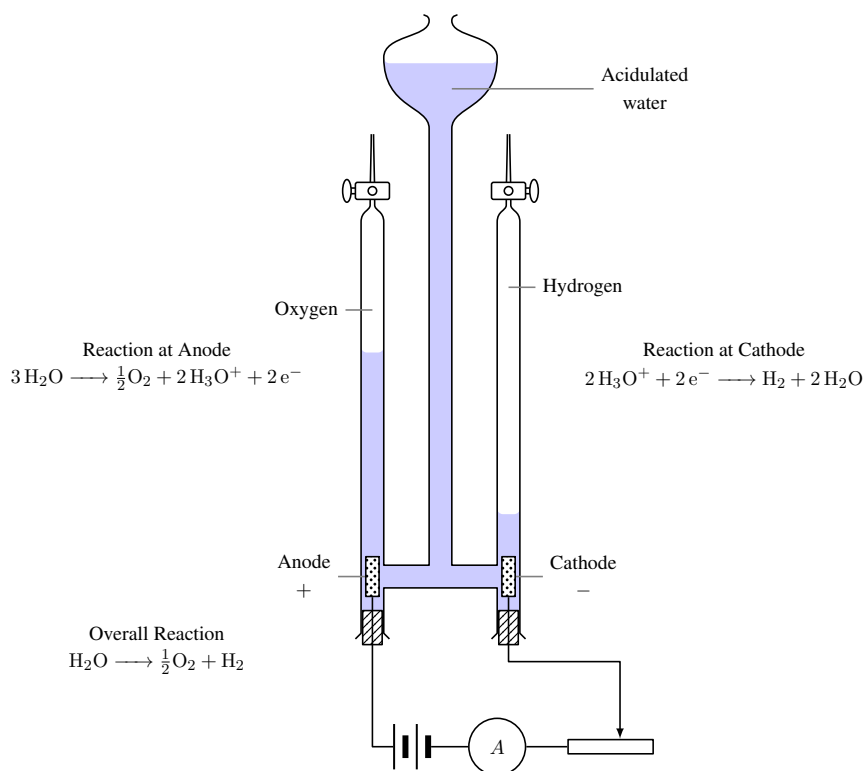
Overall, the potential needed to split water is -2.06V. However, this number is calculated at standard conditions, and at neutral PH one needs a more positive value (close to 1.2V). Still, electrochemical processes are affected by overvoltage. That means that in order to electrolyze water we need more than 1.2V, being the difference between the needed value and the value calculated using electrochemistry the overvoltage or overpotential. This effect is due to electron transfer limitations from the solution to the electrode that increases the measured voltage needed. At the same time, pure water does not contain enough ions to conduct the electricity and in order to foster the flow of electricity, we need to add ions in the form of an acid or an electrolyte.

Electrolysis and ion mixtures Electrolysis is used to plate metal surfaces in a setup in which we have a solution containing a mixture of ions and by applying an external voltage one of the metals is deposited. Normally, the voltage is increased from zero and the first ions to deposit are those with higher-more positive–standard reduction potential. For example, in a mixture of Na^+ ($\mathcal{E}°$-=2.71V), Au^+ ($\mathcal{E}°$=1.52V) and Pt^{2+} ($\mathcal{E}°$=1.2V), gold would be plated first.

Electrolysis applications Electrolysis is a technique extensively used in the chemical industry to obtain metals from its ores. Metals are electron-rich elements with an excellent reducing character. In contact with the atmosphere, they are found in nature in the form of ores, a mixture of oxides, sulfides, and silicates. Electrolysis can be used to return oxidized metals into their original metallic state. Here we will describe the electrolytic production of aluminum, and chlorine, as well as other applications of electrolysis such as the electrorefining of metals and metal plating. Aluminum is a very abundant element on earth. Still, back in the 18th century, pure aluminum was a rare and expensive metal worth more than \$1000000 a pound. In nature, it is found in the form of an oxide, bauxite–the name of this mineral comes from a french region Le Baux, near Marseille in the south. This mineral is a mixture of aluminum oxide (called silica), mixed with iron oxide, silicon oxide, titanium oxide as well as other silicates. However, the production of aluminum from bauxite was proven to be very difficult. In the late nineteenth century, a french and an American scientist independently developed an electrolytic method to produce aluminum, the Hall-Heroult. On one hand, bauxite cannot be electrolyzed in water as water is more reducing than aluminum and in an aluminum solution, water would electrolyze rather than aluminum. On the other hand, in order to electrolyze bauxite, it needs to be melted first in order for the ions to migrate in the electrolytic cell, and the melting point of this mineral is close to 2050°C. The method consists first of the purification of aluminum oxide by treating bauxite with sodium hydroxide. The resulting sludge contains dissolved aluminum oxide that is then acidified with carbon dioxide. The resulting hydrated alumina is then treated with molten cryolite (Na_3AlF_6) in order to reduce the melting point of the oxide to 1000°C. The electrolysis of this melted mixture produces ultrapure–close to 100% –aluminum, that deposits on the bottom of the cell, as Al is denser than the oxide mixture. In the cell, a large current flow of 250000A is applied to a series of graphite rods. Carbon

dioxide forms in the anode. Chlorine gas is used during sanitation for the disinfection of water. It is also used as a bleaching agent during the production of paper and in the manufacturing of many household cleaning products. Several electrolytic cells are used for the production of chlorine. First, the Downs cell employs a mixture of melted sodium chloride and calcium chloride to produce gaseous chlorine and solid sodium as a byproduct. Calcium chloride reduces the melting point of sodium chloride (close to $800°C$) to $600°C$. The generated sodium–a very reactive metal–needs to be kept under oil to avoid its oxidation. Chlorine can also be produced from brine, an aqueous solution of sodium chloride. In this process, sodium hydroxide contaminated with sodium chloride is produced as a byproduct. The mercury cell eliminated this problem hence producing cleaner sodium hydroxide. In this cell, mercury is used as the cathode for the electrolytic treatment of brine. In the anode, chlorine is generated. In the cathode, sodium is reduced instead of water, producing a solid solution of mercury and sodium that is then treated with water producing sodium hydroxide and hydrogen gas, while recovering mercury. Other applications of electrolysis are the electrorefining of metals. Impure metals are often produced from the treatment of metal ores. A way to purify these is by using the impure slabs as anodes in electrolytic cells with an aqueous solution of the metal to be refined, where metals are dissolved into ions. Impurities and noble metals deposit on the bottom of the cell in the form of sludge. The cathode contains a slab of pure metals that grows as dissolved ions deposit in the pure metal slab forming an ultrapure metallic layer. Another useful electrolytic application is metal plating. For example, tin cans are made of tin-coated steel and car bumpers are often chrome-plated steep parts. Metals can be plated by means of an electrolytic cell in which the metal to be plated is placed in the cathode and the liquid solution contains ions of the plating materials. The following diagram displays the experimental set up for the electrolysis of water in which oxygen is produced in the anode and hydrogen in the cathode.

Acidulated water

Oxygen

Hydrogen

Reaction at Anode
$$3\,H_2O \longrightarrow \tfrac{1}{2}O_2 + 2\,H_3O^+ + 2\,e^-$$

Reaction at Cathode
$$2\,H_3O^+ + 2\,e^- \longrightarrow H_2 + 2\,H_2O$$

Anode
$+$

Cathode
$-$

Overall Reaction
$$H_2O \longrightarrow \tfrac{1}{2}O_2 + H_2$$

A

8.9 Corrosion

Metals corrode when returning to their original state as found in nature, in the form of oxides, sulfides, silicates, and carbonates. This complex mixture of solids is called ore. When a metal corrodes, it oxidizes. Corrosion has a severe impact on the value and properties of metals, as rusted metals often lose their integrity. Metals corrode when they oxidize, producing rust. Most structural and decorative metals (e.g. Ag, Fe, Ni, Cu, etc) spontaneously rust. They have a reduction potential lower than that of oxygen gas ($\mathcal{E}° = 1.2$V), which means they have a stronger tendency to become oxidized while oxygen reduces to water–they have a strong reducing capacity. Cooper forms Platina, a greenish copper carbonate. Silver forms silver tarnish, a silver sulfide (Ag_2S). Rust is a hydrated iron(II) oxide of complex composition ($Fe_2O_3 \cdot nH_2O$). Zinc forms a mixture of oxide and carbonate coatings. Gold is the only metal that does not oxidize under normal conditions, due to its high redox potential ($\mathcal{E}° = 1.5$V). As metals oxidize very easily under atmospheric conditions, a thin layer of rust–a coating–prevents the complete oxidation of the metal as they have a higher–less negative–reduction potential. For example, metallic aluminum ($\mathcal{E}° = -1.7$V) is naturally coated with aluminum oxide (Al_2O_3). This oxide ($\mathcal{E}° = -0.6$V) passivates the metal preventing its further oxidation. Still, this protective effect is not infallible as natural coatings are irregular and they scale off exposing the uncorroded metal to the air. Oxygen and moisture, among other factors, are responsible for the corrosion of iron. The corrosion of iron can be understood by thinking more about the functioning of a galvanic cell than on a pure oxidation process. Some areas of an iron surface are more easily oxidized than others, due to a lack of homogeneity. These areas are called anodic areas, and metallic iron oxidizes there forming iron(II) as well as electrons, which can flow in the metal. Iron(II) ions can also migrate on the surface of iron due to moisture that acts as a salt bridge. Moisture is critical for the corrosion of iron as it is necessary for ionic migration. The presence of other electrolytes such as sodium chloride can also favor the corrosion of iron due to the formation of complex iron compounds. For example, it is well known that salt on the road favors the corrosion of cars and that cars decay faster in humid weather. In the cathodic regions, iron(II) reacts with oxygen and moisture to produce rust, iron oxide. The degree of hydration of the oxide affects the color of rust, varying from black, to yellow or red. The anodic regions and cathodic regions are not necessarily close to each other. That is why rust grows in remote areas from the metal pits that start the corrosion. There are several methods to prevent corrosion. The application of coatings in the form of paints, metal plating, galvanization, or alloying can help prevent corrosion. Cr and Sn are used to plate still as they form regular and durable oxide coatings. Zn is used to galvanize iron, as Zn has a stronger tendency to be oxidized than iron. Cr and Ni are alloyed with steel to produce stainless steel. Another method to prevent corrosion is called cathodic protection. When connecting a metal that needs to be protected to a more reducing metal, a metal that can be oxidized easily, the more reducing metal acts as the anode, oxidizing first while protecting the less reducing metal. This technique is used to protect ship's hulls or steel in pipelines.

8.10 Batteries

Batteries are portable sources of electrical power. They consist of a series of galvanic cells connected in series so that the overall voltage results from the added voltage of the small cells. They are used to power a variety of essential devices, from small electric calculators
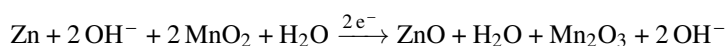
to large electric cars.

Lead batteries have been extensively used in car manufacturing since the early twenty century to self-start cars. These large and heavy batteries function under a wide range of temperatures and harsh conditions on the road, with a useful life of between 3 to 5 years. Each battery typically contains six galvanic cells, each giving about 2V, combined with an overall high voltage of about 12V. The anode is made of a lead grid, whereas the cathode is made of a metallic lead grid, coated with lead(II) oxide. Both electrodes are submerged in a sulfuric acid solution. When the battery works sulfuric acid is consumed, whereas water is being consumed as the battery charges. Traditional batteries require the periodic addition of water. The density of the sulfuric acid solutions gives an estimate of the battery conditions, as the sulfuric density decreases with use. When cars run, an alternator is used to electrolyze the battery, forcing current during recharging. One of the side reactions occurring when jump-starting the car is the electrolysis of water producing oxygen and hydrogen, which can cause battery explosions. The approximate redox reaction behind this battery is given below:

$$Pb_{(s)} + PbO_{2(s)} + 2\,H^+_{(aq)} + 2\,HSO_4^-{}_{(aq)} \xrightarrow{2\,e^-} 2\,PbSO_{4(s)} + 2\,H_2O_{(l)} \qquad \mathcal{E}^\circ = 2V$$
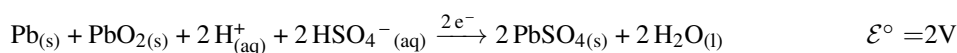
One of the drawbacks of the lab battery is its weight and the fact that contains a corrosive liquid that can leak. Dry cells are a type of battery that does not contain any liquid solution, invented more than 100 years ago. They can be found in two versions, the acid version, and the alkaline or basic version which indeed last longer. The acidic dry cell with giving an estimate of 1.5V is made of a zinc inner case acting as anode and a carbon rod in contact with a moistened mixture of MnO_2 and NH_4Cl acting as a cathode.

$$Zn + 2\,NH_4^+ + 2\,MnO_2 \xrightarrow{2\,e^-} Zn^{2+} + Mn_2O_3 + 2\,NH_3 + 2\,H_2O$$
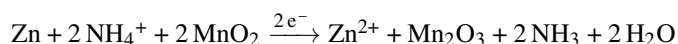
The alkali version used KOH or NaOH to replace NH_4Cl.

$$Zn + 2\,OH^- + 2\,MnO_2 + H_2O \xrightarrow{2\,e^-} ZnO + H_2O + Mn_2O_3 + 2\,OH^-$$

The zinc anode corrodes less rapidly in basic–alkaline–conditions. Other dry cells are the silver cell, the mercury cell, and the rechargeable nickel-cadmium battery. The silver cell is made of Zn anode and Ag_2O under basic conditions as a cathode. Mercury cells are made of a Zn anode and HgO in a basic environment as the cathode. The Ni-Cd batteries are made of a Cd anode and a NiO_2 cathode.The approximate redox reaction behind this battery is given below:

$$Cd_{(s)} + NiO_{2(s)} + 2\,OH^-_{(aq)} + 2\,H_2O_{(aq)} \xrightarrow{2\,e^-} Cd(OH)_{2(s)} + Ni(OH)_{2(s)} + 2\,OH^-_{(s)}$$
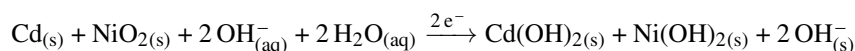
A remarkable type of battery is the lithium-ion batteries used in rechargeable cellphones and laptops. One of the first designs contained $LiCoO_2$ dopped with numerous transition metals and LiC_6. When the battery is used–on discharge–Lithium ions (Li^+) migrate from the anode to the cathode where they intercalate in the solid electrode, whereas electrons circulate to the anode in the external circuit. The opposite process happens during the charge. Fuel cells are a special type of battery in which reactants are continuously supplied in the form of a gas. In hydrogen fuel cells, hydrogen is being reduced in the anode to produce water and oxygen is being oxidized in the cathode.