1 Electrochemistry

© PxFuel

GOALS

1. Identify anodes/cathodes
2. Calculate cell potentials
3. Interpret the line notation
4. Calculate cell potentials of concentration cells
5. Relate cell potential with $\Delta G°$

BATTERIES 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.

1.1 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.

`Discussion:` What is the difference between a battery and a galvanic cell?

`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 charge 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) with an electrolyte solution (e.g. $H^{+}_{(aq)}$). Electrodes without a metall being directly involved in the redox reaction need to include an external metall 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 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.

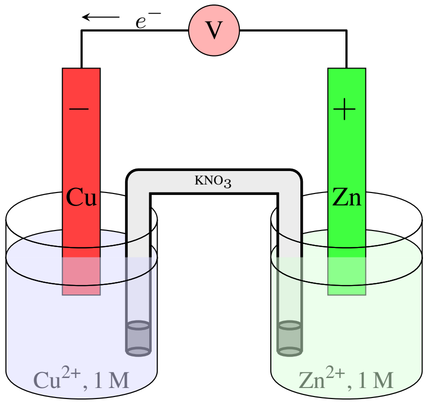
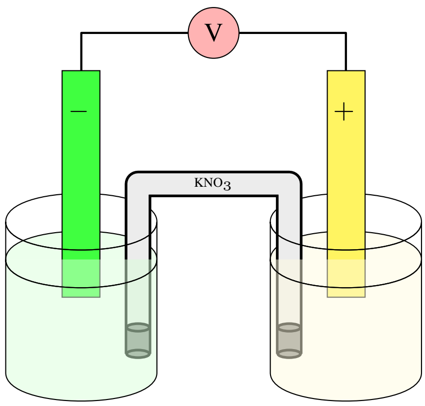


Figure 1.1 The Daniell galvanic cell

`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

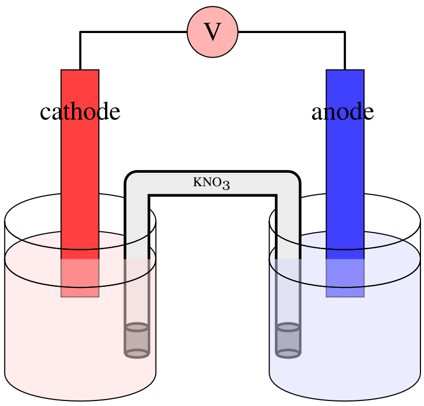


SOLUTION

(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



1.2 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 single 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:

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

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 $\mathcal{E}^\circ$, where the symbol $^\circ$ represents standard state. At the same time, every redox reaction can be written as a reduction or an oxidation reaction. As we tabulate standard electrode potentials, all reactions will be written as reduction reactions and the standard potentials are called standard reduction potential $\mathcal{E}^\circ$.

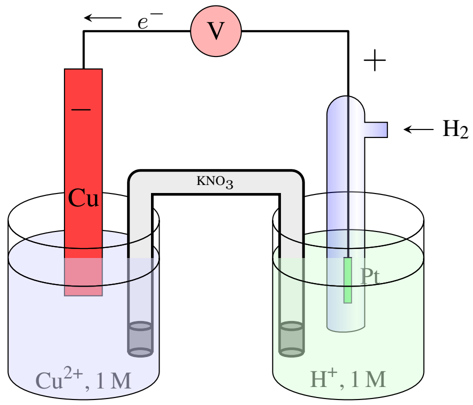


Figure 1.2 A galvanic cell with a hydrogen anode and a copper cathode. The hydrogen electrode is the reference electrode with null electrodic voltage. Hence the voltage of this cell will directly give the copper electrode voltage.

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:

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

How to determine which electrode will act as an anode and which will act as the 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:

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

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

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

Differently, inverting the reduction reaction switches the sign of the reduction potential. For example, the standard reduction potential of Titanium(II) is -1.63V

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

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

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

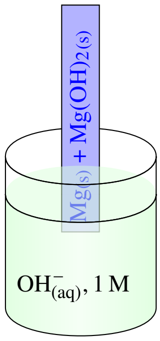
Sample Problem 2

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 1.1 Standard reduction potentials at 298K

Element	Reaction	$\mathcal{E}^\circ$ (V)	Element	Reaction	$\mathcal{E}^\circ$ (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	$Ag_2S_{(s)} + 2e^- \rightleftharpoons 2Ag_{(s)} + S_2-_{(aq)}$	-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)

Increasing oxidizing strength (decreasing reducing strength)

1.3 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:

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

We want to will 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:

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

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).

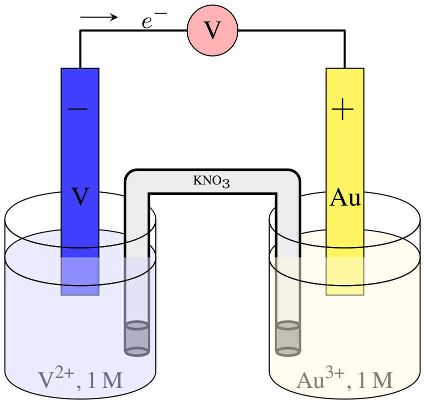


Figure 1.3 A Au-V galvanic cell

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:

$$3\,V_{(s)} + 2\,Au^{3+}_{(aq)} + 6\,e^- \rightleftharpoons 3\,V^{2+}_{(aq)} + 2\,Au_{(s)}{}^+ 6\,e^- \qquad \text{-}\mathcal{E}^\circ_{anode} = 1.13+1.52=2.65V$$

The following equation is used to calculate the cell voltage from the separate electronic potentials:

$$\boxed{\mathcal{E}^\circ_{cell} = \mathcal{E}^\circ_{cathode} - \mathcal{E}^\circ_{anode}} \tag{1.1}$$

Electrons flowing The number of electros flowing in a galvanic cell–specifically the moles of electros flowing–deppends on the electrons produced in the anode and consumed in the cathode. Givem 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 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,

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

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

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

Now we can add both reaction:

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

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

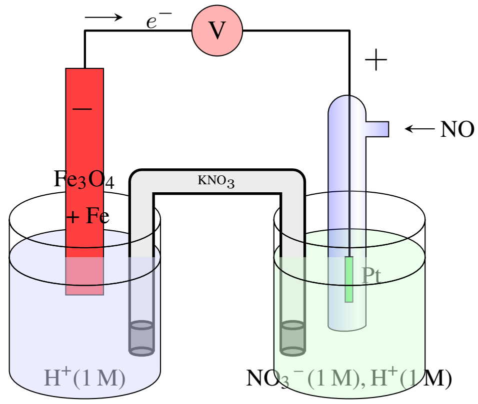
We would have to remove water molecules as they appear in both sides and protons as well: $8\,NO_3{}^-{}_{(aq)} + \; + 9\,Fe_{(s)} + \; + \cancel{24\,e^-} \rightleftharpoons 8\,NO_{(g)} +$

$$+ 4\,H_2O_{(l)} + 3\,Fe_3O_{4(s)} + H_{(aq)}{}^+ + \cancel{24\,e^-} \qquad \mathcal{E}^\circ_{cell}$$

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.

$$Cr^{3+} + e^- \rightleftharpoons Cr^{2+} \qquad \mathcal{E}^\circ = -0.42V$$

$$Cu^+ + e^- \rightleftharpoons Cu_{(s)} \qquad \mathcal{E}^\circ = 0.52V$$

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

1.4 Line notation for galvanic cells

There is a quick and easy way to represent a galvanic cell without having to draw the whole cell set up. 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:

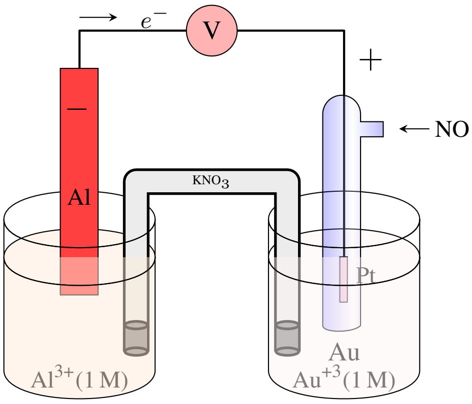
$$Zn \,|\, Zn^{2+}(1\ M) \,||\, Fe^{2+}, Fe^{3+}(1\ M) \,|\, Pt$$

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:



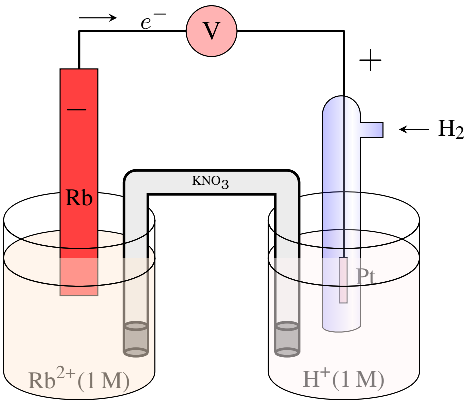
SOLUTION

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:



1.5 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:

$$\boxed{w_{max} = -n_e \cdot F \cdot \mathcal{E}_{cell}} \tag{1.2}$$

where:

n_e is the number of moles of electrons flowing through the cell

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

$$\boxed{\Delta G^\circ = -n_e \cdot F \cdot \mathcal{E}^\circ_{cell}} \tag{1.3}$$

where:

n_e is the number of moles of electrons flowing through the cell

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

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

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

$$3\,V_{(s)} + 2\,Au^{3+}_{(aq)} + 6\,e^- \rightleftharpoons 3\,V^{2+}_{(aq)} + 2\,Au_{(s)} + 6\,e^- \qquad \mathcal{E}^\circ_{cell} = 2.65V$$

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:

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

The negative sign in the Formula 1.3 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 1.3 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 1.3, as these do not function reversibly. Finally, there exist an equivalent formula to Formula 1.3 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:

$$2\,Au^+ + Ni_{(s)} \rightleftharpoons 2\,Au_{(s)} + Ni^{2+} \qquad \mathcal{E}^\circ_{cell} = 2.08V$$

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:

$$\boxed{\ln K = \frac{n_e \cdot F \cdot \mathcal{E}^\circ_{cell}}{RT}} \tag{1.4}$$

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:

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

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 lower 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.

1.6 Electrochemical series: dissolving metals in acid

When a metal dissolves it becomes ions. In other words, a dissolving metal is part of a redox reaction in which a metallic element transforms into its ionic state. During this process, on one hand, the metal loses electrons while producing cations and hence the metal is being oxidized. On the other hand, the solvent becomes reduces. Acids contain protons that can be reduced to produce hydrogen. This way, 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. In particular, 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:

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

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_2O and Ag^+/Ag. We have that the reduction potentials are:

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

We have that the larger $\mathcal{E}^\circ$ the stronger the oxidizing character. Hence, the pair O_2/H_2O 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

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

The reduction potential of zinc is smaller than the reduction of protons. This means that hydrogen has a stronger tendency to reduced than zinc, 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 an element will dissolve in simple nonoxidizing acids (e.g. HCl). If the redox potential of the metal is lower than zero then the metal will dissolve. For example, aluminum, lead, or iron will dissolve in HCl. Differently, gold or silver will not. We have called HCl a nonoxidizing element. Other acids such as HNO_3 are called oxidizing acids. This is because its reduction potential is higher than zero, and as such, they have a stronger capacity to oxidize metals than hydrochloric acid. Still, we can find out whether gold or silver will be dissolved in nitric acid by comparing both redox pairs:

$$Au^+ + e^- \rightleftharpoons Au_{(s)} \qquad \mathcal{E}_1^\circ = +1.83V$$

$$Ag^+ + e^- \rightleftharpoons Ag_{(s)} \qquad \mathcal{E}_2^\circ = +0.80V$$

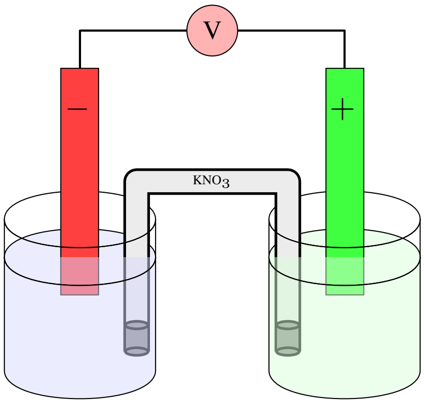
$$NO_3{}^-{}_{(aq)} + 2\,H^+ + e^- \rightleftharpoons NO_{2(g)} + H_2O \qquad \mathcal{E}_3^\circ = +0.80V$$

We have that nitroc acid will dissolve silver ($\mathcal{E}_2^\circ \simeq \mathcal{E}_3^\circ$) but not gold ($\mathcal{E}_1^\circ > \mathcal{E}_3^\circ$).

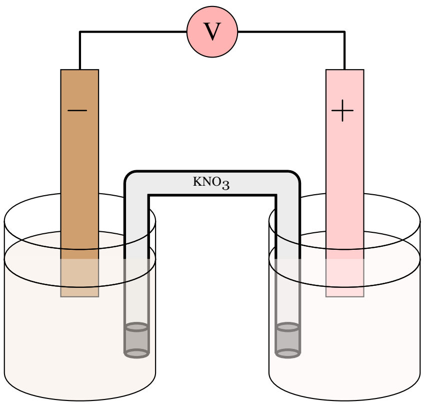
CHAPTER 1

Introduction to galvanic cells

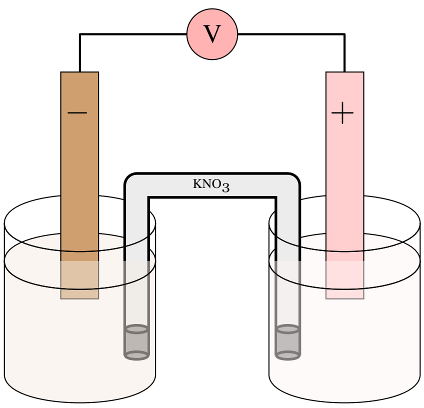
1.1 For the galvanic cell below, indicate: (a) the direction of flow of electrons (b) the direction of flow of cations (c) the direction of flow of anions



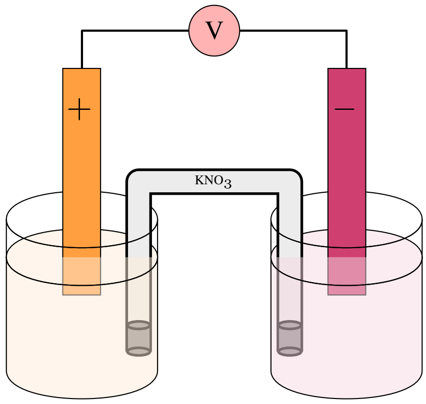
1.2 For the galvanic cell below, indicate: (a) the direction of flow of electrons (b) the direction of flow of cations (c) the direction of flow of anions



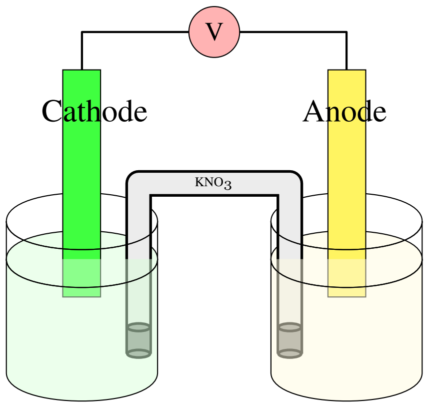
1.3 For the galvanic cell below, indicate: (a) label the anode (b) label the cathode



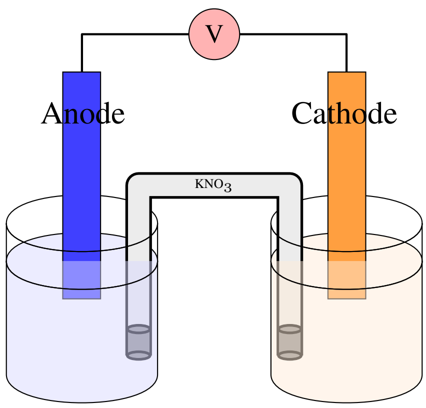
1.4 For the galvanic cell below, indicate: (a) label the anode (b) label the cathode



1.5 For the galvanic cell below, indicate: (a) label the sign (− or +) of each electrode (b) identify the flow of electrons



1.6 For the galvanic cell below, indicate: (a) label the sign (− or +) of each electrode (b) identify the flow of electrons



STANDARD REDUCTION POTENTIALS

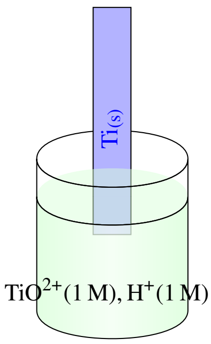
1.7 Sketch a semi-cell for the semi reaction below, indicate if the electrode is a solid-liquid electrode or gas-liquid electrode. Assume standard conditions:

$$Ni^{2+}_{(aq)} + 2\,e^- \rightleftharpoons Ni_{(s)}$$

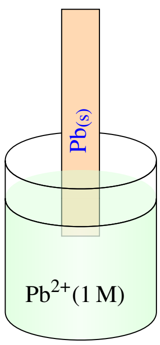
1.8 Sketch a semi-cell for the semi reaction below, indicate if the electrode is a solid-liquid electrode or gas-liquid electrode. Assume standard conditions:

$$MnO_4{}^- + 8\,H^+ + 5\,e^- \rightleftharpoons Mn_2{}^+ + 4\,H_2O$$

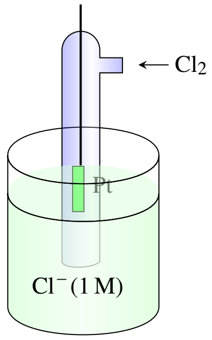
1.9 Indicate the redox reaction being the following semi-cell:



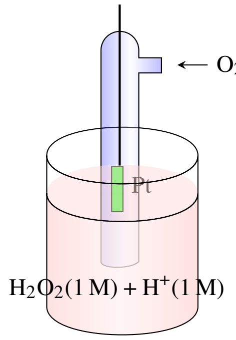
1.10 Indicate the redox reaction being the following semi-cell:



1.11 Indicate the redox reaction being the following semi-cell:



1.12 Indicate the redox reaction being the following semi-cell:



1.13 Sketch a galvanic cell based on the overall redox reaction shown below:

$$2\,I_{2(s)} + 2\,Al_{(s)} \rightleftharpoons 6\,I-_{(aq)} + 2\,Al^{3+}_{(aq)}$$

1.14 Sketch a galvanic cell based on the overall redox reaction shown below:

$$2\,MnO_4{}^-{}_{(aq)} + 16\,H_{(aq)}{}^+ + 5\,Ti_{(s)} \rightleftharpoons 2\,Mn^{2+}_{(aq)} + 8\,H_2O_{(l)} + 5\,Ti^{2+}_{(aq)}$$

REDOX REACTIONS IN GALVANIC CELLS

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

$$Li^+ + C_{6(s)} + e^- \rightleftharpoons LiC_{6(s)} \qquad \mathcal{E}^\circ = -2.84V$$

$$N_{2(g)} + 2\,H_2O + 6\,H^+ + 6\,e^- \rightleftharpoons 2\,NH_4OH_{(aq)} \qquad \mathcal{E}^\circ = +0.09V$$

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

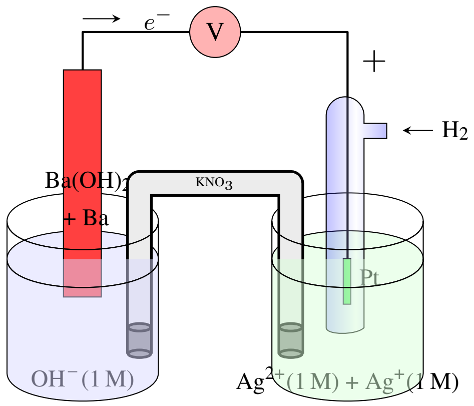
1.16 We want to build up a galvanic cell based on the reactions below.

$$Cr^{3+} + e^- \rightleftharpoons Cr_2{}^+ \qquad \mathcal{E}^\circ = -0.42V$$

$$AgO_{(s)} + 2\,H^+ + e^- \rightleftharpoons Ag^+ + H_2O \qquad \mathcal{E}^\circ = +1.77V$$

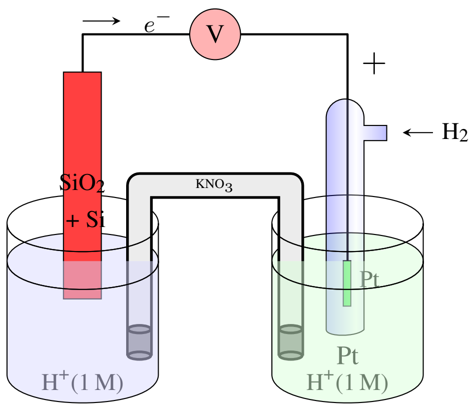
Indicate: (a) the anodic and cathodic reactions (b) the balanced overall redox (c) the number of electrons flowing (d) the overall voltage of the cell

1.17 For the galvanic cell below



Indicate: (a) Identify the anodic and cathodic reactions (b) Indicate the anodic and cathodic standard reduction potential(c) Indicate the overall potential of the cell (d) Indicate the number of electrons flowing

1.18 For the galvanic cell below



Indicate: (a) Identify the anodic and cathodic reactions (b) Indicate the anodic and cathodic standard reduction potential (c) Indicate the overall potential of the cell (d) Indicate the number of electrons flowing

1.19 For the unbalanced reaction below, calculate $\mathcal{E}°$ and indicate whether the reaction is spontaneous under standard conditions. Balance the reaction.

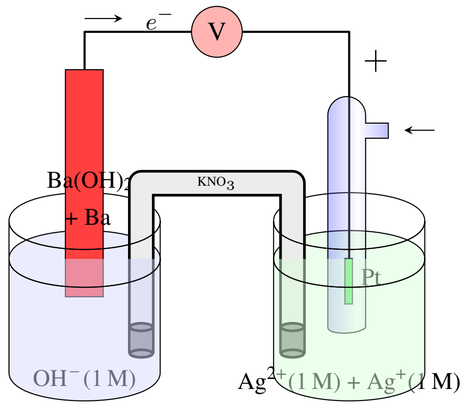
$$Zn_{(s)}{}^{+} Au^{+} \rightleftharpoons Au_{(s)} + Zn^{2+}$$

1.20 For the unbalanced reaction below, calculate $\mathcal{E}°$ and indicate whether the reaction is spontaneous under standard conditions. Balance the reaction.

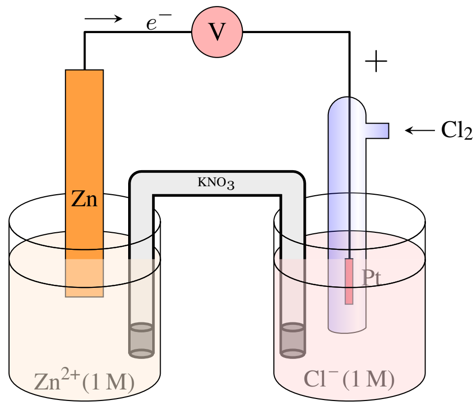
$$2\,HMnO_4{}^{-} + Fe_2O_{3(s)} + \rightleftharpoons 2\,Fe^{2+} + 2\,MnO_4{}^{-}$$

Line notation for galvanic cells

1.21 Give the line notation for the galvanic cell below:



1.22 Give the line notation for the galvanic cell below:



1.23 Calculate the standard cell potential for the galvanic cell below:

$$Zn\,|\,Zn^{2+}(1\,M)\,||\,Cl^{-}\,(1\,M)\,|\,Cl_2(1atm)\,|\,Pt$$

1.24 Calculate the standard cell potential for the galvanic cell below:

$$Fe\,|\,Fe^{3+}(1\,M)\,||\,HMnO_4{}^{-}(1\,M) + 3\,H^{+}(1\,M)\,|\,MnO_2$$

Cell potential, Gibbs free energy, and equilibrium constant

1.25 Answer the following questions:(a) Calculate the standard reduction potential for the Li/Li^{+} pair given that the standard formation Gibbs free energy of formation Li^{+} is 193KJ/mol. (b) Calculate the standard reduction potential for the Na/Na^{+} pair given that the standard formation Gibbs free energy of formation Na^{+} is 261KJ/mol.

1.26 Answer the following questions:(a) Calculate the standard reduction potential for the Al/Al^{+3} pair given that the standard formation Gibbs free energy of formation Al^{+3} is 480KJ/mol. (b) Calculate the standard reduction potential for the Ti/Ti^{+2} pair given that the standard formation Gibbs free energy of formation Ti^{+2} is 314KJ/mol.

1.27 Calculate the standard Gibbs free energy for the following electrochemical reaction:

$$FeO_2^{4-} + 8\,H^+ + 3\,e^- \rightleftharpoons Fe_3^+ + 4\,H_2O \quad \mathcal{E}^\circ = 2.20V$$

1.28 Calculate the standard Gibbs free energy for the following electrochemical reaction:

$$Fe_3O_{4(s)} + 8\,H^+ + 2\,e^- \rightleftharpoons 3\,Fe^{2+} + 4\,H_2O \; \mathcal{E}^\circ = 0.98V$$

1.29 Calculate the standard Gibbs free energy for the following reaction using the given electrochemical data:

$$2\,Cr_{(s)} + 3\,I_{2(s)} \rightleftharpoons 2\,Cr^{3+} + 6\,I^-$$

$\mathcal{E}^\circ$ ($Cr^{3+}/Cr_{(s)}$)=-0.74V and $\mathcal{E}^\circ$ ($I_{2(s)}/I^-$)=0.54V.

1.30 Calculate the standard Gibbs free energy for the following reaction using the given electrochemical data:

$$2\,Fe_{(s)}{}^+ \, 3\,H_2O_{2(aq)} + 6\,H^+ \rightleftharpoons 6\,H_2O + 2\,Fe^{3+}$$

$\mathcal{E}^\circ$ ($Fe^{3+}/Fe_{(s)}$)=-0.04V and $\mathcal{E}^\circ$ ($H_2O_{2(aq)}/H_2O_{(l)}$)=1.78V.

ELECTROCHEMICAL SERIES: DISSOLVING METALS IN ACID

1.31 From the following list indicate the metals that can be dissolved in HCl in standard conditions: (a) Sr (b) Ba (c) Ag (d) Pt

1.32 From the following list indicate the metals that can be dissolved in HCl in standard conditions: (a) Ti (b) Cr (c) Cd (d) Cu

Answers **1.1** (a) left to right (b) left to left side of salt bridge (c) right to right side of salt bridge **1.2** (a) right to left (b) right to right side of salt bridge (c) left to left side of salt bridge **1.3** (a) left (b) right **1.4** (a) right (b) left **1.5** (a) left $+$, right $-$ (b) from right to left **1.6** (a) right $+$, left $-$ (b) from left to right **1.7** A solid-liquid electrode with a metallic Ni piece in contact with a Ni(II) 1M solution **1.8** A solid-liquid electrode with a metallic Pt piece in contact with a Mn(II) and permanganate 1M solution **1.9** $TiO^{2+} + 2H^+ + 4e^- \rightleftharpoons Ti_{(s)} + H_2O$ **1.10** $Pb^{2+} + 2e^- \rightleftharpoons Pb_{(s)}$ **1.11** $Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-$ **1.12** $O_{2(g)} + 2H^+ + 2e^- \rightleftharpoons H_2O_{2(aq)}$ **1.13** not given **1.14** not given **1.15** (a) anode ($Li^+ + C_{6(s)} + e^- \rightleftharpoons LiC_{6(s)}$);cathode($N_{2(g)} + 2H_2O + 6H^+ + 6e^- \rightleftharpoons 2NH_4OH_{(aq)}$) (b) $N_{2(g)} + 2H_2O + 6H^+ + 6e^- + 6LiC_{6(s)} \rightleftharpoons 2NH_4OH_{(aq)} + 6Li^+ + 6C_{6(s)} + 6e^-$ (c) 6 (d) 2.93V **1.16** (a) anode ($Cr^{3+} + e^- \rightleftharpoons Cr_2{}^+$);cathode($AgO_{(s)} + 2H^+ + e^- \rightleftharpoons Ag^+ + H_2O$) (b) $AgO_{(s)} + 2H^+ + e^- + Cr_2{}^+ \rightleftharpoons Ag^+ + H_2O + Cr^{3+} + e^-$ (c) 1 (d) 2.19V **1.17** (a) anode($Ba(OH)_2 + 2e^- \rightleftharpoons Ba_{(s)} + 2OH^-$);cathode($Ag^{2+} + e^- \rightleftharpoons Ag^+$) (b) anode(-2.99);cathode(1.98) (c) 4.97V (d) 2 **1.18** (a) anode($SiO_{2(s)} + 4H^+ + 4e^- \rightleftharpoons Si_{(s)} + 2H_2O$);cathode($2H^+ + 2e^- \rightleftharpoons H_{2(g)}$) (b) anode(-0.91);cathode(0.00V) (c) 0.91V (d) 4 **1.19** $\mathcal{E}°$=2.59V, spontaneous; $Zn_{(s)}{}^+ 2Au^+ \rightleftharpoons 2Au_{(s)} + Zn^{2+}$ **1.20** $\mathcal{E}°=-0.17$V, nobspontaneous; $2HMnO_4{}^- + Fe_2O_{3(s)} + 6H^+ \rightleftharpoons 2Fe^{2+} + 3H_2O + 2MnO_4{}^- + 2H^+$ **1.21**

$$Ba, Ba(OH)_2 \mid OH^-(1\ M) \parallel Ag^{2+}, Ag^+(1\ M) \mid Pt$$

1.22

$$Zn \mid Zn^{2+}(1\ M) \parallel Cl^-\ (1\ M) \mid Cl_2(1atm) \mid Pt$$

1.23 2.12V **1.24** 2.13V **1.25** (a) -3.04V (b) -2.71V **1.26** (a) -1.66V (b) -1.63V **1.27** -637KJ **1.28** -189KJ **1.29** -741KJ **1.30** -1053KJ **1.31** (a) Sr (b) Ba (c) Ag (d) Pt **1.32** (a) Ti (b) Cr (c) Cd (d) Cu