

1 Electrochemistry: galvanic cells

EXPERIMENT

Electrochemistry: galvanic cells

Goal

The goal of this laboratory experiment is to build up a series of galvanic cell as well as a concentration cell.

Materials

- ☐ A series of 150mL beaker
- ☐ A salt bridge
- ☐ A series of electrodes: Zn, 2 Cu electrodes, Pb, Fe, 2 graphite electrodes, Pt
- ☐ Two sets of banana plug to alligator clip wires and a voltmeter
- ☐ A series of solutions: 0.1M $\text{Cu}(\text{NO}_3)_2$, 0.1M $\text{Zn}(\text{NO}_3)_2$, 6M HNO_3 , 0.1M $\text{Pb}(\text{NO}_3)_2$, 0.05M $\text{Fe}_2(\text{SO}_4)_3$ mixed with 0.05M FeSO_4 in 1M H_2SO_4

Background

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 $\text{Cu}^{2+}_{(\text{aq})}$ ions. However, electrodes are not always made of metals. For example, electrodes can contain gas in contact (e.g. $\text{H}_{2(\text{g})}$) with an electrolyte solution (e.g. $\text{H}^{+}_{(\text{aq})}$). Electrodes without a metal 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 ($\mathcal{E}_{\text{anode}}$) is always lower than the one from the cathode ($\mathcal{E}_{\text{cathode}}$). 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.

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 $\text{Cu}_{(\text{aq})}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}_{(\text{s})}$, whereas metallic zinc is converted into zinc ions in the anode following the reaction $\text{Zn}_{(\text{s})} \longrightarrow \text{Zn}_{(\text{aq})}^{2+} + 2\text{e}^-$. 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.

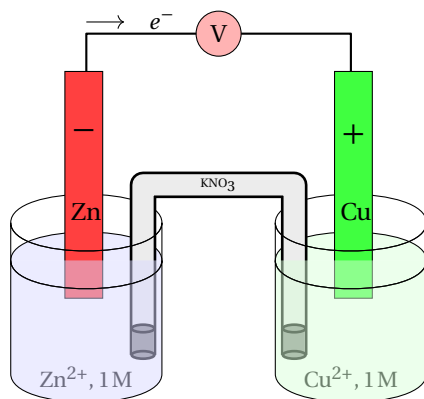


Figure 1 The Daniell galvanic cell

Anodes and cathodes

The standard reduction potential of an electrode predicts the tendency of an electrode 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:



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 :



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

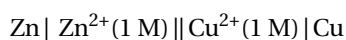


while the standard potential of oxidation of Titanium into Titanium(II) is $+1.63\text{V}$



The Nernst equation applied to a galvanic cell

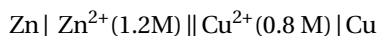
We can also apply the Nernst's equation to a galvanic cell, for example the Daniell cell:



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 :



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,



in which the following redox reaction occurs



Applying Nernst's equation at 298.15K we have:

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

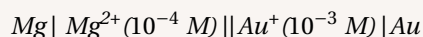
$$\Delta\mathcal{E}_{\text{cell}} = 1.10 - \frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{1.2}{0.8} = 1.09\text{V}$$

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:

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

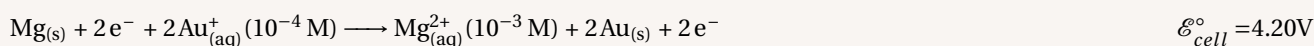
Example

For the galvanic cell below:



(a) Calculate the standard voltage of the cell, given $\mathcal{E}^\circ (\text{Au}^+/\text{Au}) = 1.83\text{V}$ and $\mathcal{E}^\circ (\text{Mg}^{2+}/\text{Mg}) = -2.37\text{V}$ (b) calculate the cell potential at 298.15K

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

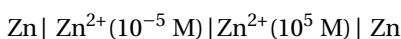


We have that two electrons flow through the cell. To calculate the cell potential at 298.15K we apply Nernst equation. While calculating Q we have to place the anodic concentration on top and the cathodic on the bottom:

$$\Delta \mathcal{E}_{cell} = \Delta \mathcal{E}_{cell}^{\circ} - \frac{R \cdot T}{n_e \cdot F} \ln Q = 4.20 - \frac{8.314 \cdot 298.15}{2 \cdot 96485} \ln \frac{10^{-4}}{(10^{-3})^2} = 4.14 \text{ V}$$

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}° and anodes with large negative \mathcal{E}° 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 Nernst 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:

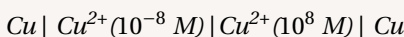


we have that $\mathcal{E}^{\circ} = +0.29\text{V}$. At the same time, good concentration cells have very low anodic concentrations and very large cathodic concentrations. For concentration cells we have that as both electrodes are made of the same material $\Delta \mathcal{E}^{\circ} = 0$. Hence, Nernst equation for a concentration cell is simplified to:

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

Example

For the concentration cell below:



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

Answer: 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, whereas 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 through the cell:

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

Table 1 Standard reduction potentials at 298K

Element	Reaction	\mathcal{E}° (V)	Element	Reaction	\mathcal{E}° (V)
↑ Sr	$\text{Sr}^+ + \text{e}^- \rightleftharpoons \text{Sr}_{(\text{s})}$	-4.10	H	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})}$	0.00
Ca	$\text{Ca}^+ + \text{e}^- \rightleftharpoons \text{Ca}_{(\text{s})}$	-3.80	Ag	$\text{AgBr}_{(\text{s})} + \text{e}^- \rightleftharpoons \text{Ag}_{(\text{s})} + \text{Br}^-$	+0.07
Li	$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}_{(\text{s})}$	-3.04	S	$\text{S}_4\text{O}_2^{6-} + 2\text{e}^- \rightleftharpoons 2\text{S}_2\text{O}_2 - 3$	+0.08
Cs	$\text{Cs}^+ + \text{e}^- \rightleftharpoons \text{Cs}_{(\text{s})}$	-3.03	N	$\text{N}_{2(\text{g})} + 2\text{H}_2\text{O} + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{NH}_4\text{OH}_{(\text{aq})}$	+0.09
Ca	$\text{Ca}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Ca}_{(\text{s})} + 2\text{OH}^-$	-3.02	Hg	$\text{HgO}_{(\text{s})} + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Hg}_{(\text{l})} + 2\text{OH}^-$	+0.10
Ba	$\text{Ba}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Ba}_{(\text{s})} + 2\text{OH}^-$	-2.99	C	$\text{C}_{(\text{s})} + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{CH}_{4(\text{g})}$	+0.13
Rb	$\text{Rb}^+ + \text{e}^- \rightleftharpoons \text{Rb}_{(\text{s})}$	-2.98	Sn	$\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}_2^{2+}$	+0.15
K	$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K}_{(\text{s})}$	-2.93	Cu	$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	+0.159
Ba	$\text{Ba}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ba}_{(\text{s})}$	-2.91	Fe	$3\text{Fe}_2\text{O}_3_{(\text{s})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{Fe}_3\text{O}_4_{(\text{s})} + \text{H}_2\text{O}$	+0.22
Sr	$\text{Sr}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sr}_{(\text{s})}$	-2.90	Ag	$\text{AgCl}_{(\text{s})} + \text{e}^- \rightleftharpoons \text{Ag}_{(\text{s})} + \text{Cl}^-$	+0.22
Sr	$\text{Sr}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Sr}_{(\text{s})} + 2\text{OH}^-$	-2.88	Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})}$	+0.34
Ca	$\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca}_{(\text{s})}$	-2.87	Fe	$\text{Fe}^+ + \text{e}^- \rightleftharpoons \text{Fe}_{(\text{s})}$	+0.40
Li	$\text{Li}^+ + \text{C}_6_{(\text{s})} + \text{e}^- \rightleftharpoons \text{LiC}_6_{(\text{s})}$	-2.84	O	$\text{O}_{2(\text{g})} + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-_{(\text{aq})}$	+0.40
Na	$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}_{(\text{s})}$	-2.71	Cu	$\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})}$	+0.520
Mg	$\text{Mg}(\text{OH})_2 + 2\text{e}^- \rightleftharpoons \text{Mg}_{(\text{s})} + 2\text{OH}^-$	-2.69	C	$\text{CO}_{(\text{g})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{C}_{(\text{s})} + \text{H}_2\text{O}$	+0.52
Mg	$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}_{(\text{s})}$	-2.37	I	$\text{I}_{2(\text{s})} + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54
H	$\text{H}_{2(\text{g})} + 2\text{e}^- \rightleftharpoons 2\text{H}^-$	-2.23	Mn	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{MnO}_{2(\text{s})} + 4\text{OH}^-$	+0.595
Sr	$\text{Sr}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sr}_{(\text{Hg})}$	-1.79	O	$\text{O}_{2(\text{g})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_{2(\text{aq})}$	+0.70
Al	$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}_{(\text{s})}$	-1.66	Fe	$\text{Fe}_2\text{O}_3_{(\text{s})} + 6\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$	+0.728
Ti	$\text{Ti}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ti}_{(\text{s})}$	-1.63	Fe	$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
Ti	$\text{Ti}^{3+} + 3\text{e}^- \rightleftharpoons \text{Ti}_{(\text{s})}$	-1.37	Ag	$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}_{(\text{s})}$	+0.80
Ti	$\text{TiO}_{(\text{s})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Ti}_{(\text{s})} + \text{H}_2\text{O}$	-1.31	Hg	$\text{Hg}_2^{2+} + 2\text{e}^- \rightleftharpoons 2\text{Hg}_{(\text{l})}$	+0.80
Mn	$\text{Mn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mn}_{(\text{s})}$	-1.18	N	$\text{NO}_3^-_{(\text{aq})} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{NO}_{2(\text{g})} + \text{H}_2\text{O}$	+0.80
V	$\text{V}^{2+} + 2\text{e}^- \rightleftharpoons \text{V}_{(\text{s})}$	-1.13	Fe	$2\text{FeO}_2^{2-} + 5\text{H}_2\text{O} + 6\text{e}^- \rightleftharpoons \text{Fe}_2\text{O}_3_{(\text{s})} + 10\text{OH}^-$	+0.81
Ti	$\text{TiO}^{2+} + 2\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Ti}_{(\text{s})} + \text{H}_2\text{O}$	-0.93	Hg	$\text{Hg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Hg}_{(\text{l})}$	+0.85
Si	$\text{SiO}_{2(\text{s})} + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Si}_{(\text{s})} + 2\text{H}_2\text{O}$	-0.91	Mn	$\text{MnO}_4^- + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HMnO}_4^-$	+0.90
Fe	$\text{Fe}_2\text{O}_3_{(\text{s})} + 3\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Fe}(\text{OH})_{2(\text{s})} + 2\text{OH}^-$	-0.86	Hg	$2\text{Hg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Hg}_2^{2+}$	+0.91
H	$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})} + 2\text{OH}^-$	-0.828	Pd	$\text{Pd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pd}_{(\text{s})}$	+0.915
Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}_{(\text{s})}$	-0.762	N	$\text{NO}_3^-_{(\text{aq})} + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{NO}_{(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$	+0.96
Cr	$\text{Cr}^{3+} + 3\text{e}^- \rightleftharpoons \text{Cr}_{(\text{s})}$	-0.74	Fe	$\text{Fe}_3\text{O}_4_{(\text{s})} + 8\text{H}^+ + 2\text{e}^- \rightleftharpoons 3\text{Fe}^{2+} + 4\text{H}_2\text{O}$	+0.98
Ni	$\text{Ni}(\text{OH})_{2(\text{s})} + 2\text{e}^- \rightleftharpoons \text{Ni}_{(\text{s})} + 2\text{OH}^-$	-0.72	Br	$\text{Br}_{2(\text{aq})} + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+1.09
Ag	$\text{Ag}_2\text{S}_{(\text{s})} + 2\text{e}^- \rightleftharpoons 2\text{Ag}_{(\text{s})} + \text{S}_{2-}^2_{(\text{aq})}$	-0.69	Ag	$\text{Ag}_2\text{O}_{(\text{s})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{Ag}_{(\text{s})} + \text{H}_2\text{O}$	+1.17
Pb	$\text{PbO}_{(\text{s})} + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Pb}_{(\text{s})} + 2\text{OH}^-$	-0.58	Pt	$\text{Pt}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pt}_{(\text{s})}$	+1.188
Fe	$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}_{(\text{s})}$	-0.44	Cl	$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{ClO}_3^- + \text{H}_2\text{O}$	+1.20
Cr	$\text{Cr}^{3+} + \text{e}^- \rightleftharpoons \text{Cr}_2^+$	-0.42	O	$\text{O}_{2(\text{g})} + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.229
Cd	$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}_{(\text{s})}$	-0.40	Cl	$\text{Cl}_{2(\text{g})} + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
Cu	$\text{Cu}_2\text{O}_{(\text{s})} + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Cu}_{(\text{s})} + 2\text{OH}^-$	-0.36	Br	$\text{BrO}_3^- + 5\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{HBrO}_{(\text{aq})} + 2\text{H}_2\text{O}$	+1.45
Pb	$\text{PbSO}_4_{(\text{s})} + 2\text{e}^- \rightleftharpoons \text{Pb}_{(\text{s})} + \text{SO}_4^{2-}$	-0.36	Br	$2\text{BrO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightleftharpoons \text{Br}_{2(\text{l})} + 6\text{H}_2\text{O}$	+1.48
Pb	$\text{PbSO}_4_{(\text{s})} + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{Hg}) + \text{SO}_4^{2-}$	-0.35	Cl	$2\text{ClO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightleftharpoons \text{Cl}_{2(\text{g})} + 6\text{H}_2\text{O}$	+1.49
Co	$\text{Co}^{2+} + 2\text{e}^- \rightleftharpoons \text{Co}_{(\text{s})}$	-0.28	Mn	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}_2^+ + 4\text{H}_2\text{O}$	+1.51
Ni	$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}_{(\text{s})}$	-0.25	Au	$\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}_{(\text{s})}$	+1.52
As	$\text{As}_{(\text{s})} + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{AsH}_{3(\text{g})}$	-0.23	Pb	$\text{Pb}^{4+} + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}$	+1.69
Ag	$\text{AgI}_{(\text{s})} + \text{e}^- \rightleftharpoons \text{Ag}_{(\text{s})} + \text{I}^-$	-0.15	Mn	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_{2(\text{s})} + 2\text{H}_2\text{O}$	+1.70
Sn	$\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}_{(\text{s})}$	-0.13	Ag	$\text{AgO}_{(\text{s})} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Ag}^+ + \text{H}_2\text{O}$	+1.77
Pb	$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}_{(\text{s})}$	-0.126	O	$\text{H}_2\text{O}_{2(\text{aq})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.78
C	$\text{CO}_{2(\text{g})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCOOH}_{(\text{aq})}$	-0.11	Au	$\text{Au}^+ + \text{e}^- \rightleftharpoons \text{Au}_{(\text{s})}$	+1.83
C	$\text{CO}_{2(\text{g})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CO}_{(\text{g})} + \text{H}_2\text{O}$	-0.11	Ag	$\text{Ag}^{2+} + \text{e}^- \rightleftharpoons \text{Ag}^+$	+1.98
Fe	$\text{Fe}_3\text{O}_4_{(\text{s})} + 8\text{H}^+ + 8\text{e}^- \rightleftharpoons 3\text{Fe}_{(\text{s})} + 4\text{H}_2\text{O}$	-0.08	Mn	$\text{HMnO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{MnO}_{2(\text{s})} + 2\text{H}_2\text{O}$	+2.09
Fe	$\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe}_{(\text{s})}$	-0.04	Fe	$\text{FeO}_2^{4-} + 8\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Fe}_3^{3+} + 4\text{H}_2\text{O}$	+2.20
H	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})}$	0.00	F	$\text{F}_{2(\text{g})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{HF}_{(\text{aq})}$	+3.05


Increasing oxidizing strength (decreasing reducing strength)

Procedure

Part A: Daniell galvanic cell

- ☐ *Step 1:* – Obtain a copper and zinc electrodes, a salt bridge as well as a potentiometer.
- ☐ *Step 2:* – We use a BK Precision potentiometer: make sure the black wire is connected to the COM connection whereas the red one is connected to the Hz V Ω connection. The potentiometer has to be turned towards the right to start measuring DC. Make sure you select the scale that gives Volts (labelled as 2 in the V scale).
- ☐ *Step 3:* – Place 0.1M $\text{Cu}(\text{NO}_3)_2$ (approximately 50 mL) in one compartment of the cell and 0.1M $\text{Zn}(\text{NO}_3)_2$ in the other.
- ☐ *Step 4:* – Obtain a copper and zinc electrodes.
- ☐ *Step 5:* – Clean the electrodes by dipping them (no more than 3 seconds) into 40mL of 6M HNO_3 . You will notice that the surface of the electrodes will become bright. Rinse the electrodes with distilled water.

Good Lab Practice


 Concentrated acid can cause severe burns and ruin your clothes.

- ☐ *Step 6:* – Obtain a salt bridge as well as a potentiometer.
- ☐ *Step 7:* – Place the electrodes in separate 150-mL beakers, placing the salt bridge between both beakers. Connect each electrode to a terminal of the potentiometer.
- ☐ *Step 8:* – To find out whether the electrodes are properly connected to the potentiometer, read the voltage from the potentiometer. If the number is negative you need to switch the electrode connections.
- ☐ *Step 9:* – Record the cell potential in the results section.

Part B: A series of galvanic cell

- ☐ *Step 1:* – Obtain a platinum (or graphite), copper, iron, lead and zinc electrodes.
- ☐ *Step 2:* – Clean the electrodes by dipping them (no more than 3 seconds) into 40mL of 6M HNO_3 . You will notice that the surface of the electrodes will become bright. Rinse the electrodes with distilled water.

Good Lab Practice

 Concentrated acid can cause severe burns and ruin your clothes.

 Use gloves to handle lead solutions. Lead solutions are poisonous.

- ☐ *Step 3:* – Gather the following solutions: 0.1M $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, FeSO_4 , and an iron solution made of 0.05M FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ in 1M sulfuric acid (this last solution was made by dissolving $\text{Fe}_2(\text{SO}_4)_3$ in sulfuric acid as solvent).
- ☐ *Step 4:* – Set up the following galvanic cells, writing down in the results section its voltage. Mind you can replace Pt by graphite.

- ☐ $\text{Cu} \mid \text{Cu}^{2+}(0.1 \text{ M})$ and $\text{Pb} \mid \text{Pb}^{2+}(0.1 \text{ M})$
- ☐ $\text{Cu} \mid \text{Cu}^{2+}(0.1 \text{ M})$ and $\text{Fe} \mid \text{Fe}^{2+}(0.1 \text{ M})$
- ☐ $\text{Cu} \mid \text{Cu}^{2+}(0.1 \text{ M})$ and $\text{Pt} \mid \text{Fe}^{2+}, \text{Fe}^{3+}(0.1 \text{ M})$
- ☐ $\text{Zn} \mid \text{Zn}^{2+}(0.1 \text{ M})$ and $\text{Pb} \mid \text{Pb}^{2+}(0.1 \text{ M})$


- ☐ $\text{Zn} \mid \text{Zn}^{2+}(0.1 \text{ M})$ and $\text{Fe} \mid \text{Fe}^{2+}(0.1 \text{ M})$
- ☐ $\text{Zn} \mid \text{Zn}^{2+}(0.1 \text{ M})$ and $\text{Pt(or graphite)} \mid \text{Fe}^{2+}, \text{Fe}^{3+}(0.1 \text{ M})$
- ☐ $\text{Fe} \mid \text{Fe}^{2+}(0.1 \text{ M})$ and $\text{Pt} \mid \text{Fe}^{2+}, \text{Fe}^{3+}(0.1 \text{ M})$

- ☐ *Step 5:* – For each cell, write down the measured voltage in the Results section. Every time you change electrodes, make sure you rinse the salt bridge with water.
- ☐ *Step 6:* – If your instructor gave you an unknown, do the following: set up two copper electrodes. One copper compartment contains copper metal and 0.10 M $\text{Cu}(\text{NO}_3)_2$. The second copper compartment contains copper metal and a $\text{Cu}(\text{NO}_3)_2$ solution of unknown concentration. Measure the voltage and calculate the molarity of the unknown.

Part C: Concentration cell

- ☐ *Step 1:* – Obtain two copper electrodes, a salt bridge as well as a potentiometer.
- ☐ *Step 2:* – Clean the electrodes by dipping them (no more than 3 seconds) into 40mL of 6M HNO_3 . You will notice that the surface of the electrodes will become bright. Rinse the electrodes with distilled water.

Good Lab Practice

 Concentrated acid can cause severe burns and ruin your clothes.



- ☐ *Step 3:* – Prepare a copper diluted solution by adding 1mL of a 0.1M concentrated $\text{Cu}(\text{NO}_3)_2$ solution into a 100mL graduated cylinder. Stir well the mixture. Fill the cylinder with distilled water until you reach the 100mL mark.
- ☐ *Step 4:* – Place some of the concentrated solution in a 150-mL beaker and some of the diluted solution in the other one. Insert one copper electrode in each beaker, placing the salt bridge between both beakers. Connect each electrode to a terminal of the potentiometer.
- ☐ *Step 5:* – Record the cell potential in the results section, as well as the nature of both electrodes ($\text{Cu} \mid \text{Cu}^{2+}(0.1 \text{ M})$ and $\text{Cu} \mid \text{Cu}^{2+}(0.01 \text{ M})$) while identifying the anode and cathode.
- ☐ *Step 6:* – Add 10 drops of the concentrated 0.1M $\text{Cu}(\text{NO}_3)_2$ solution to the most diluted electrode of the cell you built up. Record the cell potential in the results section.

Part D: Electrolysis

- ☐ *Step 1:* – Obtain two graphite electrodes and a power supply (6V battery).
- ☐ *Step 2:* – Weigh 2g of KI and transfer the solid into a 250mL Erlenmeyer flask. Add 100mL of distilled water and swirl until the solid dissolves.
- ☐ *Step 3:* – Using a PH meter, measure the PH of the KI solution. Write down the value in the results section.
- ☐ *Step 4:* – Place two graphite electrodes in a 250mL beaker. Clamp the electrodes so that they don't touch each other. Use a pair of upside-down test tubes to secure the electrodes. Attach the wires to the electrodes but do not connect them yet to the battery.
- ☐ *Step 5:* – Add 30mL of the KI solution to the beaker.
- ☐ *Step 6:* – Attach the wires to the battery and record the time in the Results section. Observe the solution.
- ☐ *Step 7:* – Allow the electrolysis to run for 15 minutes.
- ☐ *Step 8:* – After the time has elapsed, remove the electrodes from the battery. Remove the electrodes and take a good look at them.
- ☐ *Step 9:* – Stir the KI solution in the beaker and using a PH meter measure the PH. Write down the results in the results section.

Calculations

- ① Write down here the measured voltage.
- ② Write down here the cathodic reaction.
- ③ Write down here the cathodic standard potential.
- ④ Write down here the anodic reaction (revert the reaction from the table of voltages).
- ⑤ Write down here the anodic standard potential.
- ⑥ Write down here the overall reaction: add the cathodic reaction and the anodic reaction.
- ⑦ Write down here the overall standard potential.
- ⑧ Elapsed time in seconds.
- ⑨ Measured PH.
- ⑩ Calculated hydroxyl concentration:

$$[\text{OH}^-] = 1 \times 10^{-14} / 10^{-PH}$$

- ⑪ Change on hydroxyl concentration:

$$\Delta [\text{OH}^-] = [\text{OH}^-]_f - [\text{OH}^-]_0$$

- ⑫ The intensity in Amperes:

$$\textcircled{11} \times 96485 / \textcircled{8}$$

STUDENT INFO

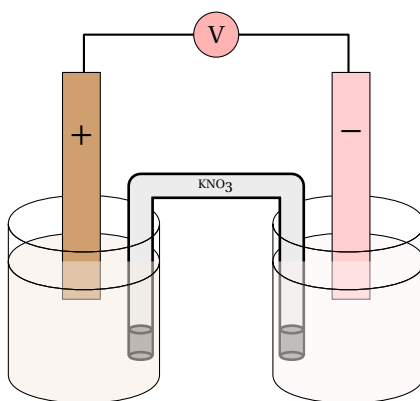
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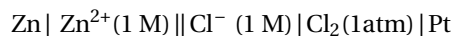
Pre-lab Questions

Electrochemistry: galvanic cells

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



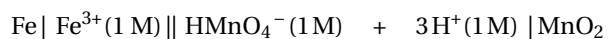
2. Calculate the standard cell potential for the galvanic cell below:



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



4. Calculate the standard cell potential for the galvanic cell below:



5. For the concentration cell below:



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

STUDENT INFO

Name:

Date:

Results
EXPERIMENTElectrochemistry:
galvanic cells

Part A						
Electrodes	$\Delta \mathcal{E}_{exp}$	Cathodic reaction	$\mathcal{E}_{cath}^{\circ}$	Anodic reaction	$\mathcal{E}_{anod}^{\circ}$	Total reaction
	①	②	③	④	⑤	⑥
Cu—Zn						⑦
Part B						
Electrodes	$\Delta \mathcal{E}_{exp}$	Cathodic reaction	$\mathcal{E}_{cath}^{\circ}$	Anodic reaction	$\mathcal{E}_{anod}^{\circ}$	Total reaction
Cu—Pb						
Cu—Fe						
Zn—Pb						
Cu—Fe ³⁺ +Fe ²⁺						

Part B						
Electrodes	$\Delta \mathcal{E}_{exp}$	Cathodic reaction	$\mathcal{E}^{\circ}_{cath}$	Anodic reaction	$\mathcal{E}^{\circ}_{anod}$	Total reaction
	①	②	③	④	⑤	⑥
Zn—Fe ³⁺ +Fe ²⁺						
Fe, Fe ²⁺ —Fe ³⁺ +Fe ²⁺						
Cu ²⁺ (0.01 M)—Cu ²⁺ (0.1 M)						
Unknown						
Cu ²⁺ (0.1 M)—						
Cu ²⁺ (Unknown) #_____)						
Part C						
Cu ²⁺ (0.01 M) *—Cu ²⁺ (0.1 M)						

* After adding 10 drops of Cu²⁺ (0.1 M)

** Use the temperature value of 298K

Part D					
P_{H_0}	P_{H_f}	[OH ⁻] ₀	[OH ⁻] _f	Δ [OH ⁻]	I
⑨	⑨	⑩	⑩	⑪	⑫

STUDENT INFO

Name:

Date:

Post-lab Questions

Electrochemistry: galvanic cells

1. Calculate the percent error between the measured voltage and the calculated one for all electrodes you measured using the formula below:

$$\%Error = \frac{|\Delta\mathcal{E}_{calc} - \Delta\mathcal{E}_{exp}|}{\Delta\mathcal{E}_{calc}} \times 100$$

Electrodes	$\Delta\mathcal{E}_{exp}$ (1)	$\Delta\mathcal{E}^\circ$ (7)	Expression for $-\frac{R.T}{n_e.F} \ln Q$ (8)	$\Delta\mathcal{E}_{calc}$ (7)+(8)	% Error
Cu—Zn					
Cu—Pb					
Cu—Fe					
Zn—Pb					
Cu—Fe ³⁺ +Fe ²⁺					
Zn—Fe ³⁺ +Fe ²⁺					
Fe, Fe ²⁺ —Fe ³⁺ +Fe ²⁺					
Cu ²⁺ (0.01 M)—Cu ²⁺ (0.1 M)					
Cu ²⁺ (0.01 M)*—Cu ²⁺ (0.1 M)					

* After adding 10 drops of Cu²⁺(0.1 M)

2. Using line notation, write down the cell with that gives the largest and the cell that gives the smallest voltage.
3. If you were given an unknown, calculate its molarity.

