Demonstration Experiments

to the oral presentation

" Electrochemistry–" A Question of Potential"

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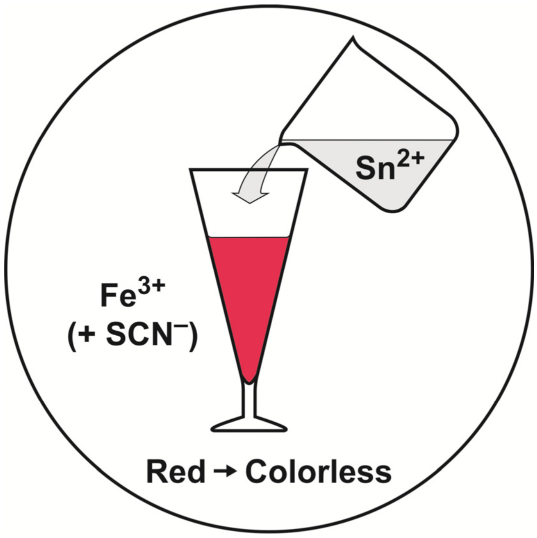
Reduction of Fe^{3+} ions by Sn^{2+} ions



Equipment:

goblet (conical cup)
glass beaker (50 mL)
graduated cylinder
dropper
glass rod

Chemicals:

iron (III) nitrate solution (approx. 0.2 kmol m^{-3})
(e.g. 20 g of $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in 250 mL of water)
acidified tin(II) chloride solution (approx. 1 kmol m^{-3})
(e.g. 5 g of $SnCl_2 \cdot 2H_2O$ dissolved in 20 mL of water and 1 mL of concentrated hydrochloric acid)
ammonium thiocyanate solution (approx. 1 kmol m^{-3})
(e.g. 7.6 g of NH_4SCN dissolved in 100 mL of water)
deionized water

Safety:

iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$):

H272, H315, H319
P302 + P352, P305 + P351 + P338

tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$):

H302, H315, H317, H319, H335
P280, P302 + P352, P305 + P351 + P338

ammonium thiocyanate (NH_4SCN):

H332, H312, H302, H412
P273, P302 + P352

It is required to wear safety glasses and protective gloves; if possible, the experiment should be carried out in a fume hood.

Procedure:

Preparation: 5 mL of the iron(III) nitrate solution is poured into the goblet and made up to 150 mL with deionized water. 20 mL of the tin (II) chloride solution is provided in the beaker.
Procedure: About 10 drops of ammonium thiocyanate solution are added to the goblet and the solution is stirred. Subsequently, the blood-red solution is mixed with the tin(II) chloride solution and stirred again.

Observation:

The strong red color disappears a few minutes after tin(II) addition.

Explanation:

The iron(III) cations react with the thiocyanate anions to form deep red colored iron(III) thiocyanate complexes. If a tin(II) solution is added to the solution containing iron(III), according to the conversion formula

$$2\ Fe^{3+}|w + Sn^{2+}|w \rightarrow 2\ Fe^{2+}|w + Sn^{4+}|w$$

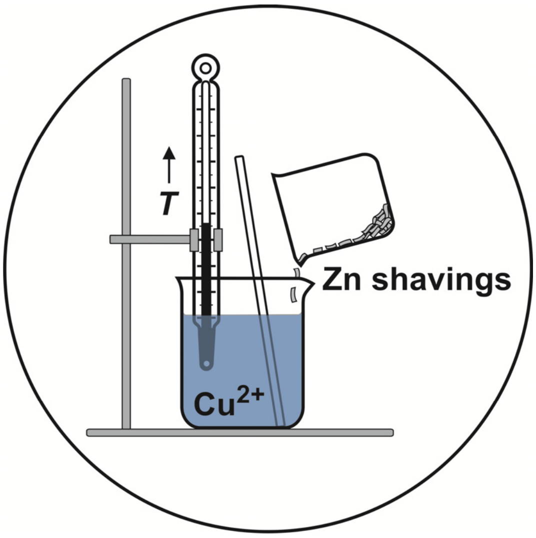
Fe^{3+} will be reduced to Fe^{2+}, while Sn^{2+} will be oxidized to Sn^{4+}, because according to the levels of the electron potentials [$\mu_e^{\ominus}(Sn^{2+}/Sn^{4+}) = -14$ kG > $\mu_e^{\ominus}(Fe^{2+}/Fe^{3+}) = -74$ kG], the redox pair Sn^{2+}/Sn^{4+} is more strongly reducing than the redox pair Fe^{2+}/Fe^{3+}. Therefore, the deep red color of the solution caused by the ferric thiocyanate complexes gradually disappears as the reaction progresses.

Disposal:

The solution is poured in a special jar for heavy metal waste disposal.

Reduction of Cu^{2+} ions by Zinc

—short-circuited DANIELL Element



Equipment:

tall form glass beaker (250 mL)
glass beaker (100 mL)
glass rod
demonstration thermometer (0 to 100°C)
ring stand, bosshead, extension clamp

Chemicals:

saturated copper sulfate solution (i.e. about 260 g of $CuSO_4 \cdot 5H_2O$ in 740 mL of water)
zinc shavings

Safety:

copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$):


H302, H315, H319, H410
P273, P305 + P351 + P338, P302 + P352

zinc shavings (Zn):

H410
P273

It is required to wear safety glasses and protective gloves; if possible, the experiment should be carried out in a fume hood.

Procedure:

Preparation: 200 mL of copper sulfate solution is poured in the tall form beaker. The demonstration thermometer is fixed with the clamp in such a way that it dips well into the solution. 18 g of zinc shavings are provided in the small beaker. The shavings should be shorter than 1 cm so that the mixture can be stirred more easily; shavings that are too long should therefore be cut into smaller pieces.
Procedure: The zinc shavings are poured into the copper sulfate solution and the mixture is then stirred vigorously.

Observation:

The zinc shavings immediately turn black and form a precipitate, which becomes rapidly more dense. The precipitate slowly turns coppery brown. Within 3 minutes, the temperature rises above 60 °C and the solution “fumes” slightly. The solution initially blue in color becomes green, brown and finally colorless.

Explanation:

If zinc shavings are added to a solution containing Cu(II) ions, according to the conversion formula

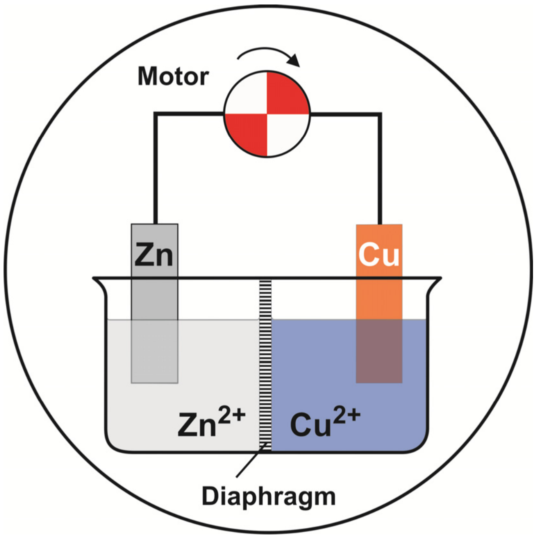
$$Cu^{2+}|w + Zn|s \rightarrow Cu|s + Zn^{2+}|w$$

Cu^{2+} will be reduced to Cu, while Zn will be oxidized to Zn^{2+}, because according to the levels of the electron potentials [$\mu_e^\ominus(Zn/Zn^{2+}) = +65.5$ kG > $\mu_e^\ominus(Cu/Cu^{2+}) = -174$ kG] the redox pair Zn/Zn^{2+} is more strongly reducing than the redox pair Cu/Cu^{2+}.

Disposal:

The solution is poured in a special jar for heavy metal waste disposal.

DANIELL Cell



Equipment:

clay flowerpot
rubber stopper
crystallizing dish
copper electrode
zinc electrode
high-impedance voltmeter
small electric motor
    with white-red card board disc
ring stand, bosshead
cables

Chemicals:

copper sulfate solution (1 kmol m^{-3})
zinc sulfate solution (1 kmol m^{-3})
saturated sodium chloride solution

Safety:

copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$):

H302, H315, H319, H410
P273, P305 + P351 + P338, P302 + P352

zinc(II) sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$):

H302, H318, H410
P280, P273, P305 + P351 + P338

It is required to wear safety glasses and protective gloves; if possible, the experiment should be carried out in a fume hood.

Procedure:

Preparation: The flowerpot, the bottom of which has been tightly sealed with the rubber stopper, is soaked from the day before in the saturated sodium chloride solution. Shortly before the experiment, it is removed from the saline solution, rinsed off and placed in the crystallizing dish. The electric motor is attached to the ring stand and the electrodes are cleaned if necessary.
Procedure: The zinc sulfate solution is filled into the crystallizing dish and the copper sulfate solution into the flowerpot. Subsequently, the copper electrode is immersed in the copper sulfate solution and the zinc electrode in the zinc sulfate solution. The electrodes are first connected to the voltmeter. Subsequently, the electric motor is connected in parallel to the voltmeter.

Observation:

A voltage of just over 1 V can be read off the voltmeter. The motor is running, clearly recognizable by the rotation of the disc; however, the voltage drops.

Explanation:

In the case of the reaction

$$Cu^{2+}|w + Zn|s \rightarrow Cu|s + Zn^{2+}|w,$$

the two half-reactions

$$Zn \rightarrow Zn^{2+} + 2\,e^{-}$$
$$Cu^{2+} + 2\,e^{-} \rightarrow Cu$$

can also be spatially separated from each other by dividing them into the two half-cells of a galvanic cell where they are connected to each other by an exterior circuit. The so-called DANIELL cell (named after the British chemist John Frederic DANIELL who invented it in 1836) is composed of a Zn and a Cu electrode that are immersed in corresponding Zn^{2+} or Cu^{2+} solutions whereby these electrolyte solutions are in contact with each other through a diaphragm. In the present experiment, the clay wall of the flowerpot assumes the role of the diaphragm.

The gradient of the chemical potential continues to drive the reaction in question, however, the reactants can no longer reach each other so easily because they are separated by a "wall" (the electrolyte solutions) that ions can permeate but electrons cannot. The only possibility is for the ions and electrons to go "separate ways." While the ions can migrate into the electrolyte solution, the electrons must be diverted through the external circuit. Zinc ions at the zinc electrode go into the solution, meaning that oxidation takes place, so we know we are dealing with an anode. The accumulation of electrons caused by the electrons left behind, gives this electrode a negative charge. At the copper electrode, on the other hand, copper ions are deposited in the form of neutral copper. This means that the ions are reduced (cathode). The "electron suction" caused by the consumption of electrons gives this electrode a positive charge. Consequently, an electric voltage develops between the two electrodes. However, immediately after even extremely small amounts of ions have transferred, electrochemical equilibrium is already established at the electrodes.

The voltage of the DANIELL cell measured in equilibrium (meaning for zero current flowing) and under standard conditions ($T^{\ominus}$ = 298 K, $p^{\ominus}$ = 100 kPa, $c^{\ominus}$ =1 kmol m^{-3}) corresponds theoretically to the difference of the redox potentials of the cathode and the anode:

$$\Delta E^{\ominus} = -U = E^{\ominus}(Cu/Cu^{2+}) - E^{\ominus}(Zn/Zn^{2+}) = +0.3402\text{ V} - (-0.7628\text{ V}) = +1.103\text{ V}.$$

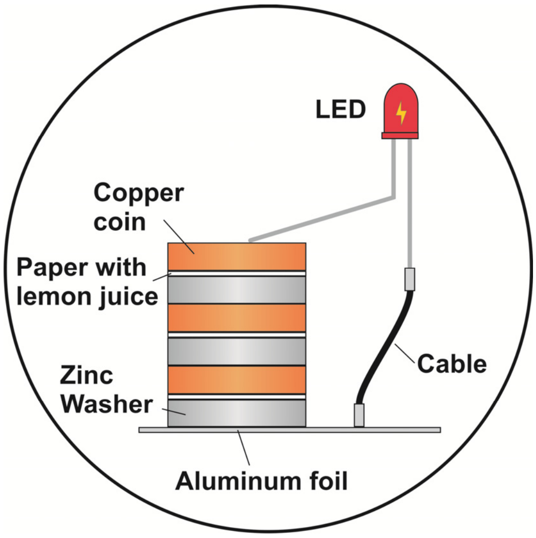
ΔE is called "reversible cell voltage" or "zero-current cell voltage."
Experimentally, an "open circuit voltage" of just over 1 V is measured.

The chemical reaction (divided into two partial reactions) can be used to drive an electron current in the external circuit. In this way, for example, a small electric motor with a white-red card board disc (to show the motion) can be driven. The DANIELL cell thus enables the direct conversion of chemical energy into electrical energy. However, the electric voltage drops when the current flows through a load because the electrochemical equilibrium is disturbed.

Disposal:

The zinc sulfate and copper sulfate solutions may be stored for further experimental purposes provided they have not been contaminated too much. Otherwise, the solutions are collected in the container for heavy metal waste.

Homemade Voltaic Pile



Equipment:

5 clean coins with copper shell of the same type
(5 Euro cent coins, US pennies, etc.)
5 zinc washers (similar diameter as the coins)
blotting paper or construction paper
aluminum foil
pencil
scissors
small plate (ceramic, plastic)
red LED (light emitting diode)
cable
alligator clip
small beaker or bowl
tweezers
paper towel
digital multimeter (optional)

Chemicals:

lemon juice

Safety:

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Procedure:

Preparation: A coin is traced 5 times on the paper with a pencil and subsequently, coin-size paper pieces are cut out. Some lemon juice is poured into the beaker or bowl. A piece of aluminum foil (about 8 x 4 cm) is folded so that it forms a strip. The longer leg of the LED is carefully bent and the shorter leg is connected to the cable by means of an alligator clip.
Procedure: The aluminum strip is placed in the middle of the plate and then a washer on the aluminum strip. A piece of paper is soaked in the lemon juice (it should be wet throughout but not dripping; if necessary it should be placed on a piece of paper towel to remove excess liquid) and laid on top of the washer. Subsequently, a coin is placed on top of the soaked paper. This pattern—washer, paper, coin—is repeated up to four times; the stack should end up with a coin.
Finally, the longer leg of the LED is held against the coin at the top of the stack and the end of the cable against the aluminum foil strip at the bottom of the stack.
Optionally, the voltage of the wet cell battery produced in this way can also be determined. For this purpose, the multimeter is set to measure DC voltage (direct current). Subsequently, the probes of the multimeter are connected to the two ends of the battery by placing one probe tip on the aluminum foil strip and the other to the coin on top of the stack.

Observation:

The LED lights up.

A voltage of about 0.8 to 0.9 V per cell (combination washer, paper, coin) can be read off the multimeter.
Remark: One should first try to make the LED light up with three cells and then with four or even five.

Explanation:

At the zinc electrode, zinc atoms dissolve into the liquid electrolyte as electrically charged ions (Zn^{2+}), leaving two negatively charged electrons (e^-) behind in the metal:

$$Zn \rightarrow Zn^{2+} + 2\ e^-.$$

Since oxidation takes place, we know we are dealing with an anode. The accumulation of electrons gives this electrode a negative charge. The Zn^{2+} ions, along with H^+ ions delivered by the acids in lemon juice (mainly citric acid), migrate through the electrolyte from the zinc to the copper electrode. At the copper electrode, two positively charged hydrogen ions (H^+) from the electrolyte accept two electrons and form hydrogen gas:

$$2\ H^+ + 2\ e^- \rightarrow H_2.$$

This means that the H^+ ions are reduced (cathode). The “electron suction” caused by the consumption of electrons gives this electrode a positive charge. Consequently, an electric voltage develops between the two electrodes which can be measured with the help of the multimeter.

When the circuit is closed by a wire, electrons are transferred from the zinc through the external circuit to copper. This electron flow can be used to make an LED light up.

Disposal:

The coins and washers can be cleaned with tap water. The paper soaked with lemon juice can be disposed of in the household waste.