IIE3

Modul Electricity II

Faraday-Constant

The purpose of this experiment is to determine the FARADAY constant with the help of a Coulomb meter. The Coulomb meter consists of three copper electrodes which are immersed in a copper sulfate solution. After an electric current was allowed to flow through the Coulomb meter for about an hour, the amount of copper transported during this time has to be determined by weighing it. From this, the FARADAY constant can be calculated.

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1.1 Preparatory questions

- What are ions, salts, bases and acids?
- Explain the terms electrolysis, electrolyte.
- What is Faraday's law?
- What is an electrochemical potential, what is a standard potential and what is a reduction potential?
- What are metals and how are they differentiated from metalloids? When is a metal a noble metal?
- Our experimental set-up enables the following half reactions among others:

  at the anode (oxidation):

$$\begin{aligned} 2SO_4^{2+} &\rightarrow S_2O_8^{2-} + 2e^- \\ 2H_2O &\rightarrow O_2 + 4H^+ + 4e^- \\ Cu &\rightarrow Cu^{2+} + 2e^- \end{aligned}$$

  at the cathode (reduction):

$$\begin{aligned} 2e^- + 2H_2O &\rightarrow H_2 + 2OH^- \\ 2e^- + 2H^+ &\rightarrow H_2 \\ 2e^- + Cu^{2+} &\rightarrow Cu \end{aligned}$$

  Why does only the final one happen in both cases?
- Would it be possible to build a Coulomb meter made of zinc and zinc electrodes instead of copper and copper electrodes?

1.2 Theory

1.2.1 Electrolysis

In liquids or gasses, unlike in solids, atoms or molecules are not at fixed positions. Therefore, the current can also be transported via charged atoms or molecules, whereas in solids, this transport usually happens via free (free moving) electrons[1]. Charged atoms or molecules are called **ions**. We distinguish

- **cations**, positively charged ions, e.g. H^+, Zn^{2+} or Cu^{2+}
- **anions**, negatively charged ions, e.g. OH^-, SO_4^{2-} or Cl^-

The anions have one or more electrons too many to be electrically neutral; the cations have one or more electrons too few. One way ions occur is by dissolving salts[2], for example:

$$NaCl \rightleftharpoons Na^+ + Cl^- \quad (1.1)$$
$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-} \quad (1.2)$$

[1] One category for solids with free electrons are metals. These kinds of substances are called first class conductors.

[2] A salt is typically a metal non-metal compound, where the bond is strongly polar (ionic; the non-metal snatches one or more electrons from the metal).

When dissolving an acid in water, ions are also produced. One or more H^+ ions (which are *de facto* protons) are split off[3], for example:

$$HCl \rightleftharpoons Cl^- + H^+ \quad (1.3)$$
$$H_2SO_4 \rightleftharpoons HSO_4^- + H^+ \quad (1.4)$$
$$HSO_4^- \rightleftharpoons SO_4^2 - +H^+ \quad (1.5)$$

This process is called **dissociation**. Quite similarly, dissolving a base leads to the formation of an OH^- ion, for example:

$$NaOH \rightleftharpoons Na^+ + OH^- \quad (1.6)$$

When dissociating water both an H^+ ion as well as an OH^- ion are formed:

$$H_2O \rightleftharpoons OH^- + H^+ \quad (1.7)$$

To sum up, ions are formed either by dissolving salts as well as by dissociation of acids and bases in water.
An **electrolyte** is what we call a fluid which conducts electrical currents. This conductivity is due to ions. As examples for electrolytes we can mention molten salts as well as water which contains solutions of salts, acids or bases. Pure water is a poor electrical conductor. While it produces ions continuously (reaction (1.7)), they keep recombining to H_2O molecules (counter reaction), such that there are only a small amount of ions in the equilibrium state ($c(H^+) \cdot c(OH^-) = 1 \cdot 10^{-14}$). Only by adding a salt or a strongly dissociating acid or base enough ions are formed to reach a good conductivity.
If an electric current is applied to an electrolyte, the ions diffuse to the *electrodes* due to electric attraction: the anions go to the anode (positive charge) where they leave behind one or more electrons, i.e. they are oxidized; the cations go to the cathode (negative charge) where they pick up one or more electrons, i.e. the cations are reduced. Thus, the electric circuit is closed. When seen from outside, electrons flow in from the anode and flow out through the cathode. The kind of chemical reaction caused by an electric charge is called **electrolysis**. As the case may be, the products of this reaction may either adhere to the electrode (e.g. when producing a silver coating through galvanization), or settle as slag, or stay dissolved or be set free as gases.
In our experiment, the OETTEL solution (copper sulfate with added sulfuric acid and alcohol) serves as electrolyte. The electrodes consist of copper. Copper is co-deposited at the cathode. New copper ions enter the solution from the anode. Therefore, the cathode becomes heavier while the anode becomes lighter. This process is illustrated in figure 1.1.

1.2.2 FARADAY's law

According to FARADAY's law, the mass transported in an electrolyte is proportional to the transported charge:

$$m = \frac{M}{z \cdot F} \cdot Q \quad (1.8)$$

The FARADAY constant is the product of the two natural constants elementary charge e[As] and AVOGADRO' constant $N_A[\frac{1}{\text{mol}}]$:

$$F = e \cdot N_A = 9.6485209 \cdot 10^4 \frac{As}{mol} \quad (1.9)$$

[3]Due to the high electronegativity of oxygen atoms, the oxygen in water molecules is partially negatively charged. This negatively charged pole is able to snatch the proton from the acids.

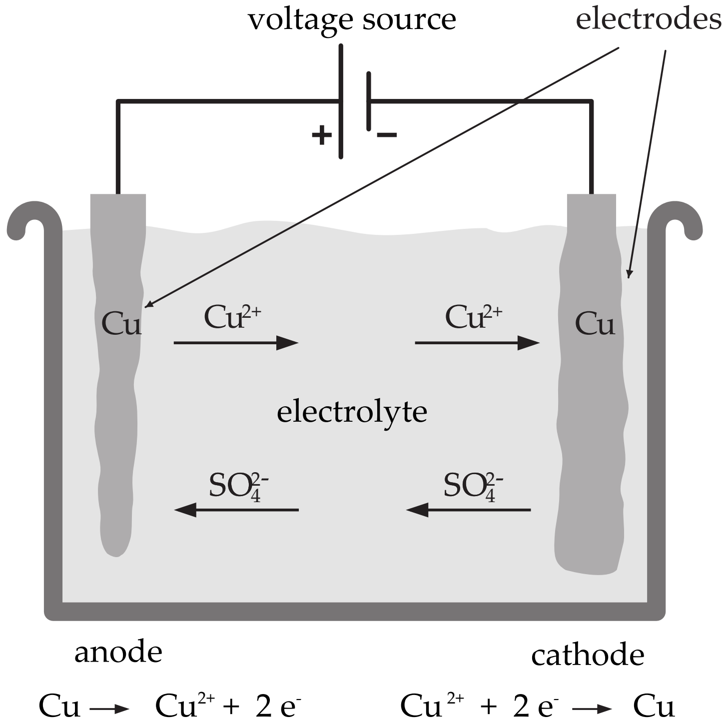

Figure 1.1: Electrolysis of copper sulfate

m $[g]$	Transported mass
M $[\frac{g}{mol}]$	Molar mass
Q $[As]$	Transported charge
z	Number of charges per molecule
F $[\frac{As}{mol}]$	FARADAY constant

1.2.3 Redox reactions, electrochemical potentials

A **redox reaction** is what we call the combination of red*uction and ox*idation. Reduction means taking on electrons, oxidation means dispensing electrons. There are always two substances involved in a redox process: one substance is oxidized, giving away one or more electrons to a second substance which is thereby reduced. For example, in the reaction

$$Zn + 2H^+ \rightleftharpoons Zn^{2+} + H_2 \qquad (1.10)$$

metallic zinc is oxidized while hydrogen ions are reduced to hydrogen gas. This reaction happens when a zinc sheet is put into a diluted[4] acid. By contrast, copper is not affected by acids. The reaction

$$Cu + 2H^+ \rightleftharpoons Cu^{2+} + H_2 \qquad (1.11)$$

does not occur. Evidently, copper is not as easily oxidized as zinc. This is due to the different electrochemical potentials of the two reactions. If a zinc electrode is submerged in a zinc sulfate solution and a copper electrode is submerged in a copper sulfate solution, connecting the two electrodes with a wire causes the copper ions to be reduced and be co-deposited at the copper electrode while the zinc electrode is oxidized and the zinc ions are dissolved. The electrons transferred in this process flow through the wire from the zinc anode to the copper cathode. The sulfations (SO_4^{2-}) do not take part in the reaction. If the copper sulfate and the

[4]dissolved in water

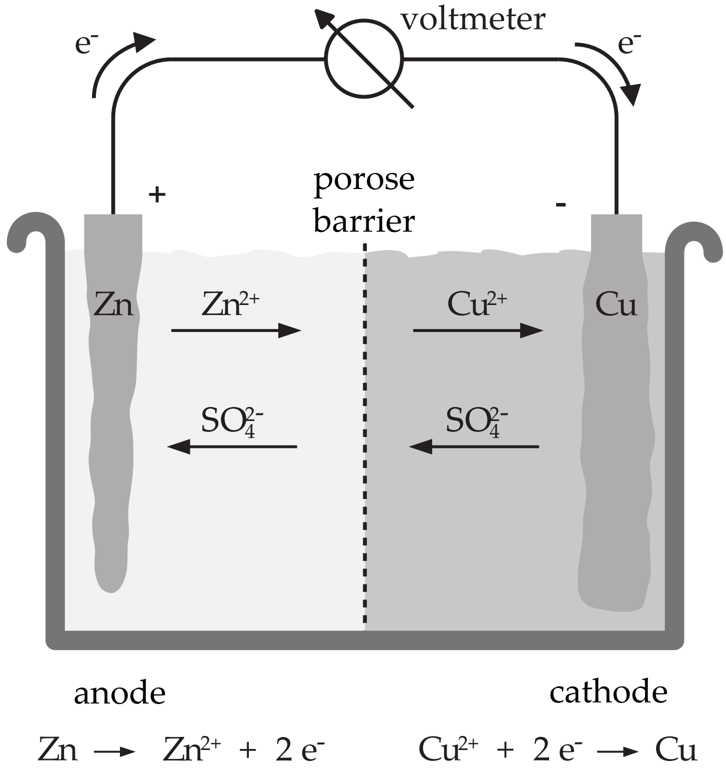

Figure 1.2: Set-up of the Daniell element

zinc sulfate are spatially separated from each other, the copper sulfate solution is negatively charged by removing Cu^{2+} ions, whereas the zinc sulfate solution is positively charged by adding Zn^{2+} ions: an electrical potential is created and grows until there is no more current flowing, which prevents further redox reactions from occurring. In order to keep the redox reaction going, the two solutions need to be connected in such a way that ion exchange is possible, but mixing[5] is not possible. One way to achieve this is by using a porous divider. Such a set-up is called Daniell element. Thus, a stable potential difference is created between anode and cathode. It can be measured with a voltmeter. The measured voltage corresponds to the difference of the **electrochemical potentials** of copper and zinc. The electrochemical potential of a substance cannot be measured absolutely, since for the measurement a second half cell with likewise unknown potential is necessary. However, the relative potential to a reference electrode can be measured.
The **Standard hydrogen electrode** serves as reference electrode. It consists of hydrogen gas which flows around a platinum electrode at a pressure of $101,3$ kPa. The electrode is submerged in an acid solution with an H^+ concentration of $c(H^+) = 1$ mol/l. The electrochemical potential between a half cell of a given substance X and the Standard hydrogen electrode is called its **standard potential**. The half cell for the standard potential consists of an electrode (reduced form of X) and a corresponding ion solution of concentration $c(X) = 1$mol/l (oxidized form of X). Apart from the concentration (or rather: from the activity), the electrochemical potential is temperature dependent. Table 1.1 lists several standard potentials at 25°C°. The given voltages refer to the reduction process (left to right), which is why they are also known as reduction potentials.

[5] if Cu^{2+} ions were to reach the zinc anode, they would oxidize the zinc directly, precluding the flow of electrons from the anode to the cathode.

Half reaction					E^0 [V]
e^-	+	Li^+	$\rightleftharpoons$	Li	− 3.045
e^-	+	Na^+	$\rightleftharpoons$	Na	− 2.714
$2e^-$	+	$2H_20$	$\rightleftharpoons$	$H_2 + 2OH^-$	− 0.82806
$2e^-$	+	Zn^{2+}	$\rightleftharpoons$	Zn	− 0.7628
$2e^-$	+	$2H^+$	$\rightleftharpoons$	H_2	0
$2e^-$	+	Cu^{2+}	$\rightleftharpoons$	Cu	+ 0.337
e^-	+	Cu^+	$\rightleftharpoons$	Cu	+ 0.521
e^-	+	Ag^+	$\rightleftharpoons$	Ag	+ 0.7991
$4e^-$	+	$4H^+ + O_2$	$\rightleftharpoons$	$2H_2O$	+ 1.229
$2e^-$	+	Cl_2	$\rightleftharpoons$	$2Cl^-$	+ 1.3595
$2e^-$	+	$S_20_8^{2-}$	$\rightleftharpoons$	$2SO_4^{2-}$	+ 2.01
$2e^-$	+	F_2	$\rightleftharpoons$	$2F^-$	+ 2.87

Table 1.1: some standard potentials

In the event that the reduction equation is supposed to be formulated as a combination of oxidation and reduction, the oxidation has to be written in opposite order (right to left). The corresponding standard potential is taken into account with opposite sign ($-E^0$). By adding the equations and the standard potentials, we get the total equation and the resulting electrochemical potential. Suppose we measure a voltage of 1.10V at the Daniell experiment:

$$\begin{array}{rrcll}
\text{Cathode:} & 2e^- + Cu^{2+} & \rightarrow & Cu(s) & E^0 = +0.34V \\
\text{Anode:} & Zn(s) & \rightarrow & Zn^{2+} + 2e^- & -E^0 = +0.76V \\
\hline
\text{Complete reaction:} & Zn(s) + Cu^{2+} & \rightleftharpoons & Cu(s) + Zn^{2+} & \Delta E^0 = +1.10V
\end{array}$$

Among all the possible reactions, only the one with the biggest ΔE^0 actually happens. If a substance is further down in the table 1.1, it is more easily reduced and thus a stronger oxidizing agent.

Reactions with $\Delta E^0 < 0$ occur in opposite direction. Thus, we can easily verify that reaction (1.10) does happen while reaction (1.11) does not. Therefore, all metals with positive standard potential are not dissolved in acid. That is why they are called **noble metals**.

In our experiment, both half cells are made of a copper anode (cathode) in copper sulfate solution, which means they are identical. The "Total reaction"

$$Cu^{2+} + Cu(s) \rightleftharpoons Cu(s) + Cu^{2+} \tag{1.12}$$

does not occur spontaneously, since $\Delta E^0 = 0$. The electrolysis is induced by applying an electrical current.

1.3 Experiment

The Coulomb meter consists of three copper electrodes, where the middle one is meant to be the cathode. A copper sulfate solution (OETTEL solution) is used as electrolyte.

1.3.1 Equipment

Component	Number
Gray plastic basin	1
Sponge	1
Stopwatch	1
Glass stirrer	1
Funnel	1
Bottle of OETTEL solution	1
copper electrodes	6
Ampéremeter	1
brown plastic basin	1
Power supply	1
Digital multimeter	1
Connecting cables (red, blue)	5

Composition of the OETTEL solution

Ingredient	Amount
Water	10 dl
Copper sulfate	125 g
Sulfuric acid	50 g
Alcohol	50 g

1.3.2 Experimental set-up

- Place the copper electrodes into the gray plastic basin and connect the cables according to figure 1.3.

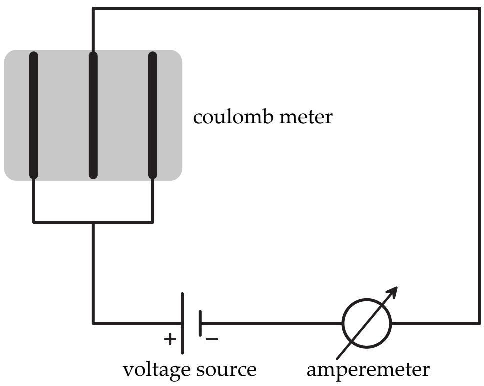

Figure 1.3: Experimental set-up

1.3.3 Tasks for the experiment

> **Be aware:**
>
> - Always wear latex gloves and protective goggles when handling OETTEL solution.
> - The current should be as high as possible, but stay below the maximum value.
> - Use the separate digital multimeter to measure the current, not the one built into the power supply.
> - While the electrolysis is happening, you should stir a little with the glass stirrer every **10** min and also adjust the current.
> - The OETTEL solution should only be filled back into the bottle by using the funnel.
> - **Caution! The OETTEL solution contains sulfuric acid. Always wear gloves and prevent contact with skin and clothing.** Wash your hands with water and soap. In case you spill something, do **not** use kitchen paper to clean it up, but use the rubber sponge.

- Determine the maximum permissible current. Estimate the area of the cathode for this. (Front *and* backside!)
- Weigh the cathode. The scales are situated in the other lab room to the right and in the back, on top of the stone shelf.
- Put on latex gloves and protective goggles. Then fill the gray plastic tray carefully with the OETTEL solution until the electrodes are completely covered in solution.
- Turn on the power supply, start the stopwatch and adjust the current.
- Turn off the power supply after at least an hour has passed and stop the stopwatch.
- Repeat the experiment once more.
- Remove the cathode from the battery tray, wash it with water and dry it well. (First with kitchen paper, then let it dry).
- Put on latex gloves again and pour the OETTEL solution carefully back into the bottle.
- Weigh the cathode again.

1.3.4 Tasks for the analysis

1. Use FARADAY's law to determine the FARADAY constant and compare with the literature value.
2. With the Coulomb meter we are able to measure the average current more accurately than with the Ampéremeter. Calculate a correction factor α for the Ampéremeter so that

$$I_{corrected} = I_{displayed} \cdot \alpha \tag{1.13}$$

   yields exactly the theoretical value for F.

3. Discuss the results.