

## Determination of the standard electrode potentials of metals

(Using CASSY)

### Aims of the experiment

- To understand the generation of an electrochemical potential.
- To measure the standard electrode potentials of metals.
- To use the HydroFlex standard hydrogen electrode.

### Principles

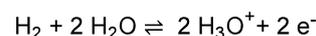
Electrochemistry deals with chemical reactions in which electrical current is generated or must be supplied. These are redox reactions, i.e. reactions in which electrons are exchanged. One reaction partner releases electrons and is oxidised, the other takes on electrons and is reduced.

Not all substances have the same tendency to release or to accept electrons. Thus, the so-called electrochemical series can be formed in which substances are arranged according to their ability to release or accept electrons.

A non-noble metal is easily oxidised and has a large tendency to dissolve if it is immersed in a solution of one of its salts. This applies to zinc, for example, with the corresponding redox pair being  $\text{Zn}/\text{Zn}^{2+}$ . The zinc adopts the form of its ions in solution. The electrode is negatively charged through the residual valency electrons. A noble metal is more easily reduced and has a greater tendency towards deposition. An example of this is copper, with the corresponding redox pair being  $\text{Cu}/\text{Cu}^{2+}$ . The Cu electrode is positively charged in a solution of one of its salts through the deposited metal ions. An electrode potential is formed in this way.

These potentials are not measurable individually. They must be determined in relationship to a second half-cell. To make the potentials comparable with one another, they are measured against the standard hydrogen electrode. In this experi-

ment, this electrode is the HydroFlex, a ready-assembled standard hydrogen electrode. Also here, sheet platinum is surrounded by hydrogen. However, a small metal hydride storage cartridge serves as a source of hydrogen. The standard electrode potential of this hydrogen electrode was set arbitrarily to 0 V in 1912. This electrode potential is based on the following reaction:



The sheet platinum is used because hydrogen itself cannot form an electrode or conduct electricity. Using the acid as an electrolyte solution enables the formation of an equilibrium between the  $\text{H}^+$  ions of the acid and the hydrogen adsorbed on the platinum.

In this experiment, the standard electrode potentials of the metals zinc and copper are determined. For this, the electrode potential is measured relative to the standard hydrogen electrode. A half-cell of a metal and the hydrogen half-cell are connected to form an electrical cell.

The potential difference indicates the difference between the deficiency of electrons on the one hand and the surplus of electrons on the other. If zinc is measured against the standard hydrogen electrode, then the tendency to dissolve is predominant in the case of zinc and the electrode acquires a negative charge. The standard hydrogen electrode has the greater ability for deposition in this case, through which it



Fig. 1: Setting up the experiment.

becomes positively charged. In the case of noble metals such as copper, the situation is reversed. The copper electrode is positively charged and the hydrogen electrode negatively charged. By definition, the standard electrode potentials of metals which release electrons to the standard hydrogen electrode are given a negative sign. In the case of metals which take on electrons from the standard hydrogen electrode, the standard electrode potentials are given a positive sign.

If the potential differences between various metals and the standard hydrogen electrode are compared, an electrochemical series of metals can be established on the basis of the standard electrode potentials determined here (see Fig. 2).

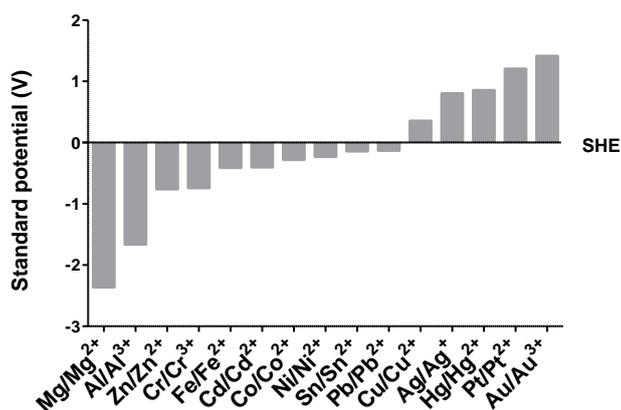


Fig. 2: Standard electrode potentials of metals compared with the standard hydrogen electrode (SHE) with the potential  $E^0 = 0.00\text{V}$ .

In this experiment, the standard electrode potentials of copper and zinc will be determined. To achieve this, they will be connected in sequence with the HydroFlex standard hydrogen electrode to form an electrochemical cell. A salt bridge filled with potassium nitrate solution provides the connection. The potentials can be read off from the Universal Measuring Instrument, Chemistry.

### Risk assessment

Contact of the metal salt solutions and the sulfuric acid with the skin should be avoided.

The solutions used in this experiment must on no account be emptied down the laboratory drain, as they are very toxic to the environment.

Potassium nitrate	
 <p><b>Signal word:</b> Caution</p>	<p><b>Hazard statements</b></p> <p>H272 May intensify fire; oxidizer</p>
	<p><b>Precautionary statements</b></p> <p>P210 Keep away from heat/sparks/open flames/hot surfaces. No smoking.</p>

Sulfuric acid, 2 N (1 M)	
 <p><b>Signal word:</b> Caution</p>	<p><b>Hazard statements</b></p> <p>H290 May be corrosive to metals. H315 Causes skin irritation. H319 Causes serious eye irritation.</p> <p><b>Precautionary statements</b></p> <p>P280 Wear protective gloves/eye protection. P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing. P337+P313 If eye irritation persists: Get medical advice/attention. P302+P352 IF ON SKIN: Wash with soap and water.</p>

Copper(II) sulfate	
 <p><b>Signal word:</b> Caution</p>	<p><b>Hazard statements</b></p> <p>H302 Harmful if swallowed. H315 Causes skin irritation. H319 Causes serious eye irritation. H302 Harmful if swallowed. H410 Very toxic to aquatic life with long-lasting effects.</p> <p><b>Precautionary statements</b></p> <p>P273 Avoid release to the environment. P305+P351+P338 If in eyes: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing P302+P352 If on skin: Wash with soap and water</p>

Zinc sulfate heptahydrate	
   <p><b>Signal word:</b> Hazard</p>	<p><b>Hazard statements</b></p> <p>H302 Harmful if swallowed. H318 Causes serious eye damage. H410 Very toxic to aquatic life with long-lasting effects.</p> <p><b>Precautionary statements</b></p> <p>P273 Avoid release to the environment. P280 Wear protective gloves/protective clothing/eye protection/face protection. P305+P351+P338 If in eyes: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing</p>

Equipment and chemicals	
1	Stand rod..... 300 41
1	Saddle base ..... 300 11
1	Bosshead S..... 301 09
1	Universal clamp 0...80 mm..... 666 555
1	Standard hydrogen electrode, HydroFlex..... 664 412
1	Container for electrodes ..... 667 4195
1	Universal Measuring Instrument, Chemistry.... 531 836
1	UIP Sensor S ..... 524 0621
4	Beaker, DURAN, 100 mL, tall..... 664 111
1	Salt bridge tube 90 mm x 90 mm ..... 667 455

1 Rubber stopper, solid, 16-21 mm diam.....	667 255
1 Plate electrode, copper, 76x40 mm, set of 10	.591 53
1 Plate electrode, zinc, 76x40 mm, set of 10	.....591 54
1 Connecting leads 19 A, 25 cm, red.....	500 4115
1 Adapter cables 2/4 mm, 30 cm, blue, set of 5..	571 26
1 Crocodile clips, polished, 6 pcs. ....	501 861
1 Measuring cylinder 100 mL, plastic base.....	665 754
1 Compact balance 200 g : 0.01 g.....	667 7977
1 Potassium nitrate, 100 g.....	672 6800
1 Copper(II) sulfate pentahydrate, 100 g.....	672 9600
1 Zinc sulfate heptahydrate, 250 g .....	675 5410
1 Sulfuric acid, dilute, c. 2 N.....	674 7920
1 Water, pure, 1L.....	675 3400

## Set-up and preparation of the experiment

### Set-up of the apparatus

1. Fix the salt bridge tube in a clamp (see Fig. 1). For this, insert a stand rod into a saddle base and screw together tightly.
2. A bosshead can now be attached to the stand rod, which is used to hold a universal clamp. Fix the salt bridge into the universal clamp.

### Preparing the solutions

1. 1 M solutions will be prepared.
2. Calculate the quantities of copper(II) sulfate pentahydrate and zinc sulfate heptahydrate to be weighed. The amount required for 50 mL is fully adequate.
3. The molar masses of both substances are required for the calculation.

$$M(\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}) = 249.69 \text{ g/mol}$$

$$M(\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}) = 287.53 \text{ g/mol}$$

Also a 1 M  $\text{KNO}_3$  solution is required for the salt bridge.

$$M(\text{KNO}_3) = 101.11 \text{ g/mol}$$

4. The calculation is performed according to the following formula:

$$m = c \cdot V \cdot M$$

5. From this, the following weights are obtained for  $V = 50 \text{ mL}$  of a  $c = 1 \text{ M}$  solution:

$$m(\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}) = 12.49 \text{ g}$$

$$m(\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}) = 14.38 \text{ g}$$

For the salt bridge ( $V = 100 \text{ mL}$ ,  $c = 1 \text{ M}$ , potassium nitrate):

$$m(\text{KNO}_3) = 10.01 \text{ g}$$

6. Dissolve the weighed amounts in the appropriate volumes of distilled water.

### Preparation of the standard hydrogen electrode

1. The standard hydrogen electrode must be commissioned before the first use. For this, set the adjustment disk to a value between 0 and 1 using an Allen key (3 mm). Be sure to note the date of commissioning.
2. Finally, allow the standard hydrogen electrode to stand for 60 minutes in a beaker filled with distilled water. After 60 minutes have elapsed, it is possible to see the escaping hydrogen.
3. To ensure the longest possible useful life, set a duration of use of 12 months using an Allen key.
4. Now, to be quite sure, place the HydroFlex standard hydrogen electrode in a beaker filled with water for a further 24 hours. The standard hydrogen electrode should then be stored in the most frequently used electrolyte in a transport container for pH electrodes, for example.

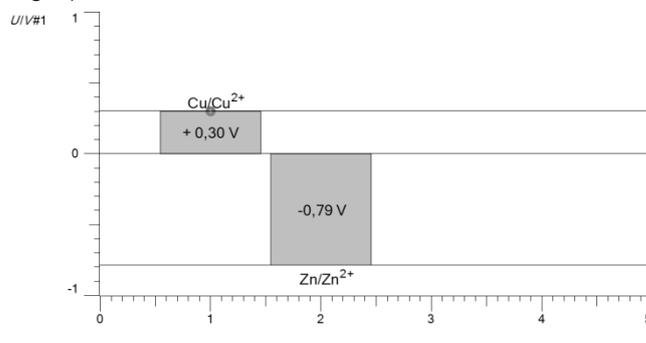
## Performing the experiment

1. Place the metal electrodes into the beakers containing the relevant solutions and the standard hydrogen electrode into a beaker containing about 50 mL of 1 M sulfuric acid. These are the prepared half-cells.
2. Fill the salt bridge with the 1 M potassium nitrate solution up to the base of the stopper and close the tube with a stopper.
3. Lower the salt bridge into the hydrogen and the copper half-cells so that it is well immersed in both solutions.
4. Plug the UIP Sensor into the Universal Measuring Instrument, Chemistry. Switch on the instrument.
5. For voltage measurement  $U$ , connect the standard hydrogen electrode to the blue voltage input socket on the UIP Sensor using the blue cable.
6. Connect the copper electrode to the red input socket on the UIP Sensor using a crocodile clip on the red connecting cable.
7. When a constant value has been reached, note this.
8. Repeat the measurement with zinc. To do this, first remove the salt bridge from the beaker with copper, quickly dab it and immerse in the beaker with the zinc electrode.
9. Record the value again.

*Note: Alternatively, the measurement values can also be recorded and displayed in the CASSY Lab software. The measurements can also be easily made with a Sensor-CASSY or Pocket-CASSY.*

## Observation

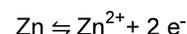
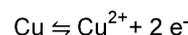
With the copper electrode a positive value is determined for the voltage, and with the zinc electrode a negative value (see Fig. 3).



**Fig. 3:** Bar graph of the two standard electrode potentials. Presentation in CASSY Lab.

## Results

The following reactions take place at the electrodes:



The standard electrode potentials obtained in the experiment are:

$$E^\circ(\text{Cu}/\text{Cu}^{2+}) = +0.30 \text{ V (literature value: } +0.34 \text{ V)}$$

$$E^\circ(\text{Zn}/\text{Zn}^{2+}) = -0.79 \text{ V (literature value: } -0.76 \text{ V)}$$

The values obtained can be compared with the known standard electrode potentials found in the literature. The measured values scarcely differ from the theoretical values. Discrepancies can even result from the environmental conditions. Standard values of electrode potentials are measured at 25 °C and 1.013 bar. A bar graph can be produced using the

CASSY Lab software (see Fig. 3). The electromotive force that would be obtained from a combination of these two half-cells can be read off directly from this graph.

**Cleaning and disposal**

The solutions used must on no account be disposed of in the laboratory drain. They must be collected in containers la-

belled for inorganic waste with heavy metals and later disposed of together with special waste. If no contamination occurred during the experiment, the solutions can be stored for future use.