

## Determination of the standard electrode potentials of metals

(Using the electrochemistry demonstration unit)

### Aims of the experiment

- To produce a standard hydrogen electrode.
- To measure the standard electrode potentials of metals.
- To carry out the electrolysis of hydrochloric acid.
- To apply redox reactions.
- To produce galvanic cells.

### 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.

However, 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

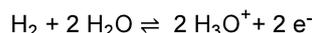
redox pair being  $\text{Zn}/\text{Zn}^{2+}$ . The zinc adopts the form of its ions in solution. The electrode is negatively charged through the residual valency electrons. A noble metal is more easily reduced and has a greater tendency to deposition. An example of this is copper, with the corresponding 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 between each other, they are measured against the standard hydrogen electrode. This consists of a platinum sheet which is surrounded by hydrogen gas. The platinum sheet is immersed in a 1 M hydrochloric acid solution. Standard values of electrode potentials are measured at 25 °C and 1.013 bar. The standard electrode



Fig. 1: Setting up the experiment.

potential of this hydrogen electrode was set arbitrarily to 0 V in 1912. The electrode potential of the standard hydrogen electrode is based on the following reaction:



The sheet platinum is used because hydrogen itself cannot form an electrode or conduct electricity. The acid is used as electrolyte solution and 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 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).

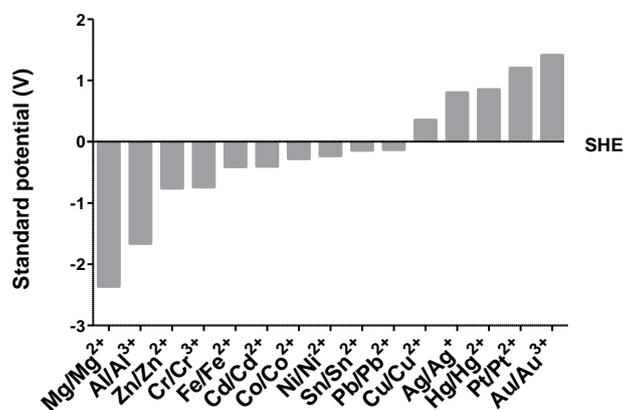


Fig. 2: Standard electrode potentials of metals compared with the standard hydrogen electrode (SHE) with the potential  $E^0 = 0.00\text{V}$ .

### Risk assessment

The hexachloroplatinic acid is toxic! Use it extremely carefully and only when wearing gloves. Skin contact with the other solutions should also 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.

<b>Copper(II) sulfate</b>	
  <b>Signal word:</b> <b>Caution</b>	<b>Hazard statements</b> 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.  <b>Precautionary statements</b> 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
<b>Hexachloroplatinic acid</b>	
   <b>Signal word:</b> <b>Hazard</b>	<b>Hazard statements</b> H301 Toxic if swallowed. H314 Causes severe skin burns and eye damage. H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled. H317 May cause allergic skin reactions.  <b>Precautionary statements</b> P260 Do not inhale dust/fume/gas/mist/vapours/spray. P301+P310 IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician. P303+P361+P353 If on skin (or hair): Remove/take off immediately all contaminated clothing. Rinse skin with water/shower. P305+P351+P338 If in eyes: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing. P405 Store locked up P501 Dispose of contents/container according to local/regional/national/international regulations.
<b>Zinc sulfate heptahydrate</b>	
   <b>Signal word:</b> <b>Hazard</b>	<b>Hazard statements</b> H302 Harmful if swallowed. H318 Causes serious eye damage. H410 Very toxic to aquatic life with long-lasting effects.  <b>Precautionary statements</b> 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

### Equipment and chemicals

1	Electrochemistry demonstration unit, CPS..664 4071
1	Electrochemistry accessories set..... 664 401
1	Panel frame C50, two-level..... 666 425
1	Table for electrochemistry, CPS ..... 666 472
3	Beaker, DURAN, 150 mL, squat ..... 602 043
1	Compact balance 200 g : 0.01 g..... 667 7977
1	Measuring cylinder 100 mL, plastic base 665 754
1	Copper(II) sulfate pentahydrate, 100 g ... 672 9600
1	Zinc sulfate heptahydrate, 250 g..... 675 5410
1	Hydrochloric acid 1 mol/L, 1 l..... 674 6910
1	Hexachloroplatinic acid, 5 g..... 672 1901
1	Water, pure, 1 L..... 675 3400

### Set-up and preparation of the experiment

#### Set-up of the apparatus

1. Insert the electrochemistry demonstration unit into the upper panel frame and supply with electrical power.
2. Place the table for electrochemistry, CPS into the frame below (see Fig. 1).

#### 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 100 mL is fully adequate.
3. The molar masses of both substances are required for the calculation.

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

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

4. The calculation for 100 mL of a 1 M solution is performed according to the following formula:

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

5. From this, the following weights are obtained:

$$m(\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}) = 24.969 \text{ g}$$

$$m(\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}) = 28.753 \text{ g}$$

6. Dissolve the weighed substances in 100 mL of distilled water.

#### Platinising the platinum mesh electrode

To be able to form a hydrogen electrode on the platinum sheet, the surface area of the platinum must be increased. This increases its ability to absorb hydrogen as well as its catalytic activity. To achieve this, platinum is deposited electrolytically onto the platinum sheet from hexachloroplatinic acid.

1. To produce the electrolyte solution, weigh 0.5 g of the liquid hexachloroplatinic acid into a 100 mL beaker and then mix in 50 mL of distilled water.
2. Now place the electrodes into the beaker. The electrodes can be degreased before the experiment using petroleum ether, for example.

The two electrodes must not touch each other under any circumstances, as this could otherwise cause a short circuit. To avoid this and to increase the fill level, a degreased glass stopper could be placed between the two electrodes.

3. Connect the two electrodes to the two outputs (5) of the demonstration unit using two cables with crocodile clips (see Fig. 3).

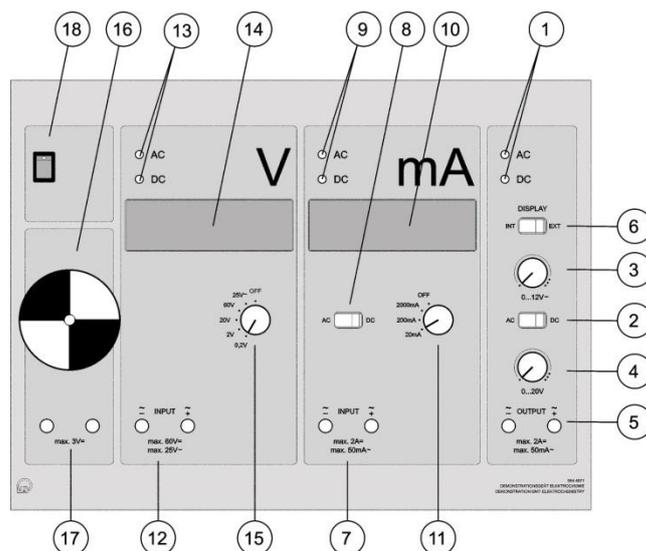


Fig. 3: The electrochemistry demonstration unit.

4. Set the changeover switch (2) to direct current, also the switch (8) on the ammeter and the rotating switch (15) on the voltmeter (the latter set to 2 V). Set switch (6) to INT to connect the power supply to the display.

5. Switch on the demonstration unit and increase the voltage by means of the rotary controller (4) until a current of about 5 - 10 mA (approx. 1.7 - 2.0 V) flows. After about 15 minutes, a blackening of the platinum mesh should already be visible.

6. From this point in time, increase the current strength over 30 minutes up to a value of about 30 mA. Gently move the beaker or one of the electrodes around from time to time to ensure that the solution is well mixed.

7. After this, the second electrode can also be platinised by swapping the poles over. When the platinisation is complete, place both electrodes into a beaker with distilled water to wash off the residual electrolyte solution.

On no account must the electrodes be directly squirt off with water, as this could cause the platinum layer to detach.

The platinisation solution produced can be used many times. To maintain the catalytic activity of the electrodes for as long as possible, they should always be stored in distilled water. The electrodes only need to be replaced when the determination of a standard electrode potential is no longer possible.

#### Preparation of the cell troughs

1. Use two cell troughs. Insert two paper membranes between the half-cell blocks of each cell trough.
2. Insert one platinised platinum electrode, each into the second outermost slot of the cell troughs. On the other side, insert a copper or zinc electrode, depending on the experiment to be performed.
3. Set the changeover switch (2) to direct current, also the switch (8) on the current meter and the rotating switch (15) on the voltage meter. To quickly switch between electrolysis and measurement, the power supply (5) and the input to the voltmeter (12) are both connected to the electrodes. Here, the platinum electrode must be connected to the negative pole of the power supply output.

#### Performing the experiment

1. Before starting the measurements, fill the half-cell with the platinum electrodes with 1 M hydrochloric acid to a depth of about 3 to 4 cm. Fill the half-cell with the copper electrode

with the copper solution and the half-cell with the zinc electrode with the zinc solution to about the same depth.

2. The electrolysis is then performed in order to generate hydrogen. For this, perform the electrolysis for about 20 - 30 seconds at about 5 V. Adjust the voltage using the rotary controller (4). The production of hydrogen can be observed at the platinum electrode.

3. Discontinue the electrolysis after the 20 - 30 seconds have elapsed. To do this, remove the cables from the output (5) of the power supply.

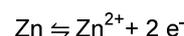
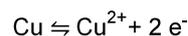
4. Read off and note down the standard electrode potential of the individual redox pairs  $\text{Cu}/\text{Cu}^{2+}$  and  $\text{Zn}/\text{Zn}^{2+}$  as soon as the voltmeter display remains constant.

### Observation

A considerable development of hydrogen can be observed during the short electrolysis time. This manifests itself in the formation of small bubbles at the platinum electrode. After removing the cables from the power supply, the voltmeter display remains constant after a brief waiting period.

### Results

The reactions that take place at the cathodes during this experiment are as follows:



The equilibrium in the case of copper lies on the side of copper, and in the case of zinc on the side of the zinc ions.

The standard electrode potentials determined in this experiment and obtained with the help of a platinised platinum electrode as a hydrogen electrode are as follows:

$$E^{\circ}(\text{Cu}/\text{Cu}^{2+}) = + 0.36 \text{ V (literature value: } + 0.34 \text{ V)}$$

$$E^{\circ}(\text{Zn}/\text{Zn}^{2+}) = - 0.73 \text{ V (literature value: } - 0.76 \text{ V)}$$

The values measured scarcely differ from the theoretical values shown in the literature.

### Cleaning and disposal

The solutions used must not be disposed of in the normal waste. They must be collected in containers labelled for inorganic waste with heavy metals and later disposed of together with special waste. They cannot be reused, as the solutions in the two cell troughs are able to mix with one another during the experiment.