Physical Chemistry

Electrochemistry

Electrochemical potentials

LD Chemistry Leaflets

C4.4.3.3a

Determination of the standard electrode potentials of non-metals

(Using the electrochemistry demonstration unit)

Aims of the experiment

- To produce a standard hydrogen electrode.
- To recognise that even non-metals form an electrode potential.
- To measure the standard electrode potentials of halogens as an example on non-metals.
- To carry out the electrolysis of various solutions.
- To apply redox reactions.

Principles

Electrochemistry deals with chemical reactions in which electrical current is generated or must be supplied. These are mostly redox reactions in which one reaction partner releases electrons and is oxidised. The other reaction partner accepts electrons and is reduced. The name redox results from the fact that both individual reactions always occur simultaneously.

Not all substances have the same tendency to release or to accept electrons. They can therefore be arranged as a series in order of voltage. The redox pairs are arranged in order of their individual standard electrode potential.

To determine the electrode potentials of corresponding redox pairs, half-cells are considered. Non-metals themselves are not electrically conductive and are often not able to form an electrode as a solid substance. This is particularly obvious with gaseous non-metals, such as the halogens. For this reason, in this experiment a graphite electrode will be immersed in the individual halogen salt solutions. The graphite electrode is electrically conductive but chemically inert. Alternatively an inert metal electrode, such as a platinum electrode, could be used. This is immersed in the relevant salt solution and is surrounded by the gas of the non-metal to be determined.

Electrode potentials can be compared with one another if they are measured with reference to the standard hydrogen electrode. This consists of a platinum sheet which is surrounded by hydrogen gas. The solution that the platinum sheet is immersed in is a 1 M hydrochloric acid solution. If standard values of the electrode potentials are to be measured, this must be done under standard conditions, i.e. at 25

Fig. 1: Set-up of the experiment.

MS-2014-08

°C and 1.013 bar. The standard electrode potential of the hydrogen electrode was set arbitrarily to 0 V in 1912. The electrode potential of the standard hydrogen electrode is based on the following reaction:

$$H_2 + 2\,H_2O \rightleftharpoons 2\,H_3O^+ + 2\,e^-$$

The sheet platinum is used because hydrogen also cannot form an electrode and does not conduct electrically. An acid serves as the electrolyte solution, so that an equilibrium can be formed between the H^+ ions of the acid and the hydrogen adsorbed on the platinum.

By definition, the standard electrode potentials of substances which release electrons to the standard hydrogen electrode are given a negative sign. In the case of substances which take on electrons from the standard hydrogen electrode, the standard electrode potentials are given a positive sign.

If one now compares the potential differences of various non-metals with the standard hydrogen electrode, an electrochemical series can be set up based on the standard potentials determined. The electrochemical series for non-metals with reference to the standard hydrogen electrode can be integrated into the electrochemical series for metals (see Fig. 2).

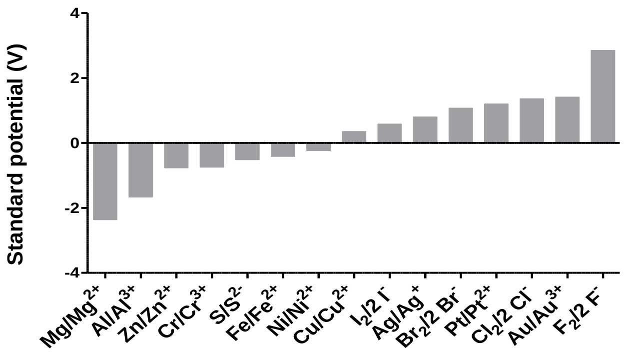

Fig. 2: Standard electrode potentials of metals and non-metals compared with the standard hydrogen electrode with the potential $E^0 = 0.00$ V.

With the help of this electrochemical series, redox reactions can be predicted and quantitative conclusions can be drawn about them. For example, it can be predicted whether a reaction will take place voluntarily or what voltage will be needed to force a reaction to take place.

In this experiment, the standard electrode potentials of the non-metals chlorine, iodine and bromine will be determined. To achieve this, they will be connected in sequence with a standard hydrogen electrode to form a electrochemical cell. All gases will be produced by electrolysis at the electrodes at the start of the experiment. This is sufficient to enable the electrode potentials to be read on the electrochemistry demonstration unit.

Risk assessment

Avoid contact of hexachloroplatinic acid with the skin! Hexachloroplatinic acid must on no account be allowed to enter the drains as it is highly toxic to the environment.

During the electrolysis of chloride, bromide and iodide solutions, the elemental halogens chlorine, bromine and iodine are produced in small amounts. Therefore only carry out the experiment in a well-ventilated place.

Hexachloroplatinic acid	
   **Signal word:** **Hazard**	**Hazard statements** 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. **Precautionary statements** 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.

Equipment and chemicals

1	Electrochemistry demonstration unit, CPS	664 4071
1	Electrochemistry accessories set	664 401
1	Panel frame C50, two-level, for CPS	666 425
1	Table for electrochemistry, CPS	666 472
4	Beaker, DURAN, 150 mL, tall	602 032
1	Compact balance 200 g: 0.01 g	667 7977
1	Measuring cylinder 100 mL, w. plastic base	665 754
1	Hydrochloric acid 1 mol/L, 1 L	674 6910
1	Sodium chloride, 250 g	673 5700
1	Potassium bromide, 250 g	672 4920
1	Potassium iodide, 50 g	672 6620
1	Hexachloroplatinic acid, 5 g	672 1901
1	Water, pure, 1L	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. For this, the amounts of sodium chloride, potassium bromide and potassium iodide to be weighed must be calculated. The amount required for 100 mL of each is fully adequate.

3. The molar masses of the substances are required for the calculation.

M(NaCl) = 58.44 g/mol
M(KI) = 166.0028 g/mol
M(KBr) = 119.002 g/mol

4. The amounts for 100 mL of 1 M solutions are calculated according to the following formula:

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

5. From this, the following weights are obtained:

m(NaCl) = 5.84 g
m(KI) = 16.60 g
m(KBr) = 11.90 g

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

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 dilute it with 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).

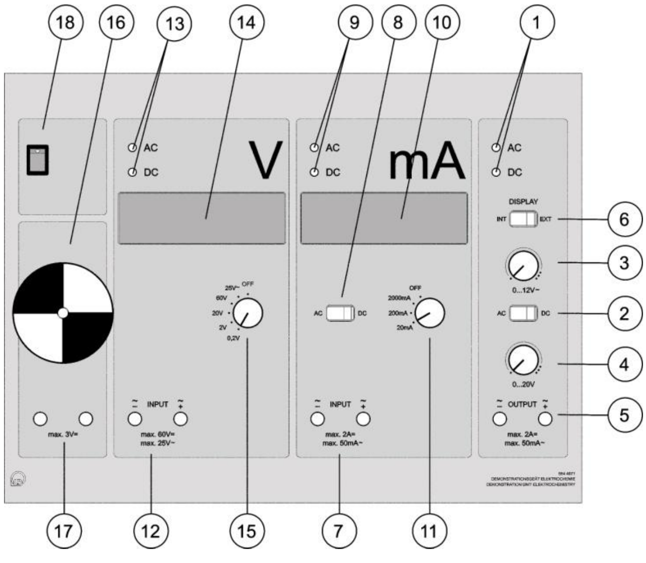

Fig. 3: The electrochemistry demonstration unit.

4. Set the changeover switch (2) to direct current, also the switch (8) on the ammeter and the rotating switch (15) on the voltmeter. 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 washed directly with a wash bottle, 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. Two cell troughs are used. 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 graphite electrode.

3. Set the changeover switch (2) to direct current, also the switch (8) on the ammeter and the rotating switch (15) on the voltmeter. 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 electrode with 1 M hydrochloric acid to a depth of about 3 to 4 cm. Fill the other half-cell first with sodium chloride solution.

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. As soon as the display on the voltmeters is constant, read off the standard electrode potential for the redox pair $Cl_2/2\ Cl^-$ and note it down.

5. Empty the cell trough and perform the measurement analogously with bromine (redox pair $Br_2/2\ Br^-$) and then with iodine (redox pair $I_2/2\ I^-$).

Observation

A considerable development of hydrogen can be observed on the side of the standard hydrogen electrode during the electrolysis. This manifests itself in the formation of small bubbles at the platinum electrode. After removing the cables from the power supply (5), the value displayed on the universal measuring instrument remains constant after a brief waiting period.

Reactions are also visible on the side of the non-metal half-cells. The smell of chlorine is noticeable during the electrolysis of the chloride solution. In the half-cell with the bromide solution, a brownish colour can be observed. In the half-cell with the iodide solution, a yellowish colour can be seen. Here we are dealing with the elemental forms of chlorine, bromine and iodine.

Results

The following reactions take place:

$$Cl_2 + 2\,e^- \leftrightharpoons 2\,Cl^-$$

$$Br_2 + 2\,e^- \leftrightharpoons 2\,Br^-$$

$$I_2 + 2\,e^- \leftrightharpoons 2\,I^-$$

Here, the equilibrium lies on the side of the molecular compounds for all non-metals.

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

$E°(Cl_2/2\,Cl^-)$ = + 1.32 V (literature value: + 1.36 V)

$E°(Br_2/2\,Br^-)$ = + 1.03 V (literature value: + 1.07 V)

$E°(I_2/2\,I^-)$ = + 0.52 V (literature value: + 0.58 V)

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

The electrode potentials of the halogens fall with increasing atomic number. The higher the atomic number of the halogen, the lower is its electrode potential, and therefore also its power of oxidation.

Cleaning and disposal

The solutions of the non-metals cannot be reused, as the solutions in the two cell troughs begin to mix with one another during the experiment. Place the remaining solutions of potassium bromide and potassium iodide into a collection container designated for inorganic salts waste for disposal. Sodium chloride solution can be disposed of in the laboratory drain.

The platinising solution can be stored in a labelled container and used again.