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# **Electrolytic deposition and quantity of electricity (Faraday's first law)** (Item No.: P1147501)

# **Curricular Relevance**



Quantity of electricity, Electrolytic deposition, Faraday law

# **Teacher information**

### **Introduction**

Already in the 19th century, Michael Faraday observed that a chemical change takes place in a current-carrying saline solution in an electrolytic cell at the electrodes. This reaction (also referred to as electrolysis), which takes place in the process, is a decomposition of a chemical compound with the aid of electrical energy. By the application of the electrical energy, redox reactions are forced, a reaction takes place at the cathode and a reaction at the anode.

The electrolysis is based on physical laws which have been observed and formulated by Faraday. These Faraday's laws describe the relationship between quantity of electricity and "deposited" quantity of substance in an electrolysis reaction. The two Faraday laws thus represent the most important laws in electrolysis.

#### **Principle**

In this experiment, the students learn the basic principles of an electrolysis reaction (1st and 2nd Faraday law). In this case, they recognize that in the electrolysis of dilute sulfuric acid, the gas volumes (oxygen and hydrogen) being formed are proportional to the time and current intensity.

In this experiment the students confirm the first Faraday law experimentally, which states that during an electrolysis reaction, the deposited mass m of a substance is directly proportional to the flow of charge (product of current intensity and time - at constant current intensity). Using this equation, the students then determine the Faraday constant F.

In the second part of the experiment, the students are concerned with the **second Faraday law,** which states that the electrochemical equivalents k (deposited mass per charge unit) behave like the equivalent masses (molar mass M divided by the valency z) of the elements. Both laws can be confirmed experimentally by water decomposition using an apparatus according to Hofmann.

# **Equipment**

The following eqipment is required for the procedure.



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**Experiment set-up**



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## **Safety information**



During the experiment all persons in the room must wear protective goggles!

#### **Safety information**

Diluted sulfuric acid has a strong irritating effect on the skin and eyes. Spray mist (on dilute sulfuric acid) irritates the respiratory organs, the mucous membranes of the upper respiratory organs being particularly affected. Do not inhale vapors (aerosols). Avoid contact with the eyes and skin. Suitable protective clothing and protective goggles should be worn during the experiment.

#### **Hazards**



#### **H- and P-statements**

Sulphuric acid, (dilute solution, 0,5 M)

● H290 May be corrosive to metals

#### Hydrogen

- H220: Extremely flammable gas
- P210: Keep away from heat/sparks/open flames/hot surfaces. No smoking
- P377: Leaking gas fire: Do not extinguish, unless leak can be stopped safely
- P381: Eliminate all ignition sources if safe to do so
- P403: Store in a well-ventilated place

#### Oxygen

- H270: May cause or intensify fire; oxidiser
- P220: Keep/Store away from clothing/.../combustible materials

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# **Introduction**

In this experiment, Faraday's laws are confirmed and the Faraday constant determined experimentally. The experimental determination takes place by the electrolysis of dilute sulfuric acid (conductivity of the distilled water would be too low, so that the electrolysis of pure water would last very long). The electrolysis is carried out in a Hofmann electrolysis apparatus, so that the gas volumes (hydrogen and oxygen) being produced during the electrolysis can be read off easily.

Faraday's laws are the most important laws which can be applied to every electrolysis, and make it possible to describe an electrolysis quantitatively. In each process, when a voltage is applied to an electrolytic solution, chemical change occurs at the electrodes in the electrolysis cell (for example, in a beaker). The formation of these substances follows Faraday's laws.

The two laws thus describe the elementary relationship between material conversions and electrical charge.

- The first Faraday law establishes a connection between the amount of a substance of a molecule deposited on an electrode and the charge (or the charge product) that is "flowed in the circuit" during electrolysis.
- The second Faraday law establishes a connection between electrochemical equivalents of substances and their equivalent masses. During an electrolysis reaction, the deposited mass m of a substance is directly proportional to the flow of charge (First Faraday's law). The second Faraday law states that the electrochemical equivalents k (deposited mass per charge unit) behave like the equivalent masses (molar mass M divided by the valency z) of the elements. Both laws can be confirmed experimentally by water decomposition using an apparatus according to Hofmann.
- The quantity of electricity, which is required in order to deposit an equivalent mass of a substance during electrolysis, is  $\bullet$ also called Faraday constant.

### **Task**

The aim of this experiment is to confirm the Faraday laws and to determine the relationships between deposited amount of substance and current strength or time as described in the introduction:

For this purpose, electrolysis of a dilute sulfuric acid is carried out at a constant current strength in the first experiment. The quantity (in a water decomposition apparatus) of gases being produced (hydrogen and oxygen) is plotted as a function of time. In the process a connection between (resulting) gas volumes and time of electrolysis is to be derived.

In the second experiment, the dilute sulfuric acid (in the electrolysis apparatus) is electrolysed for a certain time (7 minutes) at different current intensities. A connection between (generated) gas volumes and the current strength is to be derived.

In addition, the Faraday constant is determined from the measured data with the aid of the first Faraday law.



Printed: 23/08/2019 07:51:18 | P1147501

# **Set-up and procedure**

### **Set-up**

The experiment is set up as shown in Figure 1. For this purpose, the electrodes of the Hofmann electrolysis apparatus are connected to the power supply or to the multimeter to a closed circuit as shown in the figure.



Figure 1: Experiment set-up

Afterwards, the water decomposition is filled with 0.5 molar sulfuric acid and this solution is electrolysed for a few minutes with at least 200 mA. The liquid of the two limbs is saturated with the forming gases (hydrogen and oxygen) as a result. Then, the current supply is interrupted and the limbs are completely filled with liquid again by opening of the two taps.

300 mA and 30 V- should be selected for the measuring ranges of the measuring instruments (multimeter). Temperature and pressure are determined (read) with the aid of the weather monitor. These data are required then to convert the volume, which is determined under normal laboratory conditions to standard conditions (0  $\degree$  C, 1013 hPa).

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### **Procedure**

### **Experiment 1: Electrolysis at constant current intensity**

In the first experiment, it is electrolysed with closed taps (the electrolysis apparatus according to Hofmann) for 10 minutes with constant current between 200 and 300 mA. At the same time, the stopwatch is started with the beginning of the power supply. After a minute, the power supply is interrupted and the quantities of the gases being produced are read off.

The leveling bulb is displaced before until the liquid meniscus in the limb and the leveling bulb have the same height. The gas volumes being formed are recorded in a table in a dependence of time. Subsequently, the data are transferred in order to evaluate in a diagram.

### **Experiment 2: Electrolysis at constant time**

In the second experiment, it is electrolyzed in a constant period of time at different current intensities. At the start of each individual measurement, first the two limbs in the process must be completely filled with dilute sulfuric acid.

Then, electrolysis is carried out for 5 minutes at 100 mA, 200 mA and 300 mA. The corresponding hydrogen and oxygen volumes (pressure equalization by lowering the leveling bulb) are recorded in a diagram in a dependence of current intensity.



# **Observation and evaluation**

### **Observation**

The following tables show two typical measurement examples. Table 1 contains the measured values (from experimental part 1) for the dependence of the formed gas volumes at a constant current intensity. Table 2 shows the gas volumes being produced during a certain period of time (from experiment 2) at different current intensities.

#### **Observation: Electrolysis at constant current intensity**

The values in Table 1 were measured under the following conditions:  $I = 239$  mA,  $U = 15,4$  V p = 983 hPa, t = 22,3°C



#### **Observation 2: Electrolysis at constant time**

The values listed in Table 2 were measured at the following conditions:  $t = 22,3^{\circ}C$ ,  $p = 983$  hPa



## **Evaluation**

The gases produced, are hydrogen and oxygen, which are formed in the course of electrolysis, hydrogen at the cathode, and oxygen at the anode.

> $6H_2O \longrightarrow 2H_3O^+ + O_2 + 4e^-$ Anode (Oxidation, positive pole): Cathode (Reduction, negative pole):  $4H_3O^+ + 4e^- \longrightarrow 2H_2 + 4H_2O$

 $2H_2O \longrightarrow 2H_2 + 4H_2 + O_2$ Total:

### **Experiment 1: Electrolysis of dilute sulfuric acid at constant current intensity**

The evaluation of the data from the electrolysis of the dilute sulfuric acid at a constant current intensity shows that the gas volumes being produced are proportional to the time.

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Since the amount of the substance (of the formed gas) is proportional to the volume and to the mass, so the proportionality of the amount of the substance to the charge can be derived - and thus the first Faraday law

 $m = k \cdot I \cdot t$ 

with

- $\bullet$  $m =$  Mass of the deposited substance in g
- $k =$  Proportional constant, electrochemical equivalent in g/As
- $I =$  Current intensity A
- $t =$  Time in s

For the proportionality constant k (electrochemical equivalent):

$$
k = M \cdot \frac{I}{t}
$$

with

- $M$  = Molar mass of the substance in g/mol  $\bullet$
- $z =$  Charge number of the substance
- $F =$  Faraday constant  $\bullet$

With the aid of this data the Faraday constant can be determined from the first partial experiment (electrolysis at a constant current intensity). Since the measurement does not take place under standard conditions ( $0^{\circ}$ C, 1013 hPa), the volumes of the gases being produced have to be converted to the standard conditions with the following formula  $(T =$  ambient temperature in Kelvin,  $p =$  ambient pressure,  $V =$  deposited volume):

$$
V_n = \frac{273\,\mathrm{K}}{T} \cdot \frac{p}{1013\,\mathrm{hPa}} \cdot V
$$

The results from experimental part 1 are thus obtained under standard conditions

- $\bullet$  for hydrogen 16,9 ml
- for oxygen 8.2 ml  $\bullet$

The deposited masses are calculated from the corrected volumes. It is assumed that hydrogen and oxygen are approximately the same as ideal gases, and therefore the molar volume is determined for an ideal gas with the aid of the following formula.

For the deposited quantities of hydrogen and oxygen (from experimental part 1)

- $\bullet$  for hydrogen a deposited amount of 1,52 mg
- $\bullet$  for oxygen a deposited amount of 11,65 mg

Using this data, the Faraday constant F can be determined now. To do this, the first Farady's law is solved for "F", and all values being determined and calculated in the experiment are plugged in.

![](_page_7_Picture_26.jpeg)

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- For hydrogen, a value for F of 95096 As/mol can be determined (Literary value: 96487 As/mol)
- For oxygen, a value for F of 98469 As / mol can be determined (Literary value: 96487 As/mol

The corresponding electrochemical equivalent can be determined with the aid of the deposited masses of the gases (which are proportional to the respective electrochemical equivalent k) calculated above. This ensues from an easy conversion of the first Faraday law:

The following electrochemical equivalents can be determined by means of these data:

- The electrochemical equivalent for hydrogen is 0,0106 mg/As (Literary value: 0,0104 mg/As)
- The electrochemical equivalent for oxygen is 0,0813 mg/As (Literary value: 0,0813 mg/As)

#### **Experiment 2: Electrolysis of dilute sulfuric acid at a constant time**

The evaluation (diagram) of the electrolysis data of the dilute sulfuric acid at a constant time shows that the gas volumes being formed are proportional to the current intensity.

![](_page_8_Figure_10.jpeg)

The second Faraday law can be derived now from experimental parts 1 and 2. The second Faraday law states that the electrochemical equivalent k of the individual substances are in a ratio the same as their equivalent masses (molar mass M divided by the valency z)

$$
\frac{k_1}{k_2} = \frac{\frac{M_1}{z_1}}{\frac{M_2}{z_2}}
$$

If the electrochemical equivalents of hydrogen and oxygen from experiment part 1 are plugged in, or if the molar masses and the valency plugged in equation 2, so

- the ratio of the electrochemical equivalents of hydrogen to oxygen is  $1:7,7$
- the ratio of the equivalent masses is  $1: 7.9$  $\bullet$