Determining the Faraday constant

Aims of the experiment

- To perform an electrolysis.
- To understand redox reactions in practice.
- To work with a Hoffman electrolysis apparatus.
- To understand Faraday's laws.
- To understand the ideal gas equation.

Principles

When a voltage is applied to a salt or acid solution, material migration occurs at the electrodes. Thus, a chemical reaction is forced to occur through the flow of electric current. This process is called electrolysis.

Michael Faraday had already made these observations in the 1830s. He coined the terms electrolyte, electrode, anode and cathode, and formulated Faraday's laws in 1834. These count as some of the foundational laws of electrochemistry and describe the relationships between material conversions during electrochemical reactions and electrical charge. The first of Faraday's laws states that the amount of moles n, that are precipitated at an electrode is proportional to the charge that is transported through the electrolyte in the process.

$$n \text{ and } m \sim Q\text{, resp.}$$

The amount of charge Q is equal to the product of the current I and time t at a constant voltage.

$$Q = I \cdot t$$

The second law is somewhat more complex. It states that the mass m of an element that is precipitated by a specific amount of charge Q is proportional to the atomic mass, and is inversely proportional to its valence. Stated more simply, the same amount of charge Q from different electrolytes always precipitates the same equivalent mass M_e. The equivalent mass M_e is equal to the molecular mass of an element divided by its valence z.

$$M_e = \frac{M}{z}$$

In order to precipitate this equivalent mass, 96,500 Coulombs/mole are always needed. This number is the Faraday constant, which is a natural constant based on this invariability.

Now, all formulas can be combined, and the following formula is obtained, which is relates to the precipitated mass of an element during electrolysis.

$$m = \frac{I \cdot t \cdot M}{z \cdot F}$$

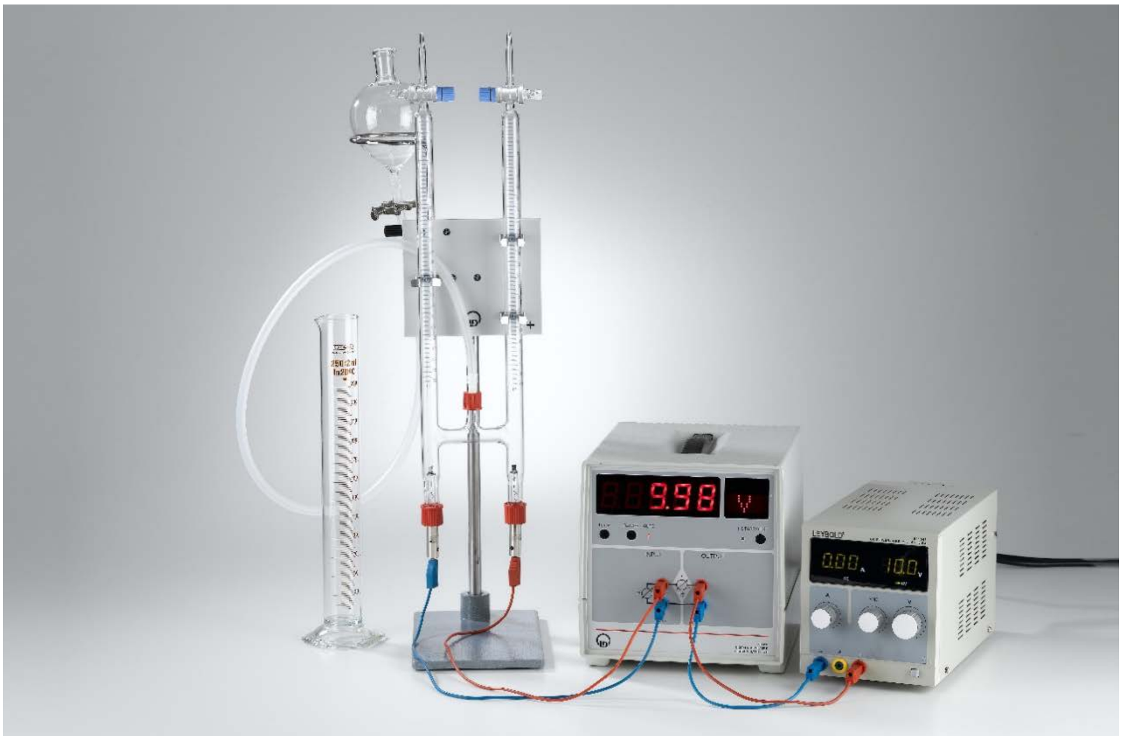

Fig. 1 Set-up of the experiment

MS-2018-07

In this experiment, the Faraday constant will be experimentally determined through the electrolysis of water. To do so, the Hoffman hydrogen electrolysis apparatus will be used.

Thus, the following reactions occur at the cathode and anode of the apparatus, respectively:

Cathode: $4\ H_3O^+ + 4\ e^- \rightarrow 2\ H_2 + 4\ H_2O$

Anode: $6\ H_2O \rightarrow 4\ H_3O^+ + O_2 + 4\ e^-$

Combined, this results in the following overall reaction.

Overall: $2\ H_2O \rightarrow 2\ H_2 + O_2$

Risk assessment

When working with sulfuric acid, protective clothing must be worn. In this experiment, pure hydrogen and pure oxygen will be generated. Wear safety goggles when exhausting the gases. Do not allow an open flame anywhere near the apparatus or when exhausting the gases.

Dil. sulfuric acid, *c* = 1 mol/l	
 **Signal word:** **Caution**	**Hazard warnings:** H315 Causes skin irritation. H319 Causes serious eye irritation. **Safety information:** P305+351+338 If in eyes: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

Equipment and chemicals

For set-up in the CPS
1 Electrolysis apparatus, CPS 666 446
1 Panel frame C50, two-level, for CPS 666 425

For the set-up using stand materials
1 Water electrolysis apparatus 664 350

For both variants:
1 Thermometer, -10...+50 °C/0.1 K...................382 35
1 DC power supply 0...16 V/0...5 A...................521 546
1 Digital mulitmeter P.......................................531 832
1 Connecting lead 19 A, 100 cm, pair 501 46
1 Connecting lead 19 A, 50 cm, pair.................501 45
1 Measuring cylinder, Boro 3.3, 100 ml.............602 953
1 Sulfuric acid, dilute, 500 ml 674 7920

Set-up and preparation of the experiment

Set-up of the apparatus

1. The apparatus is set up as can be seen in Fig. 1.
2. Insert the metal tube into the base plate and tighten.
3. Fasten the support for the apparatus onto the metal tube and place the apparatus into it.
4. Fasten the support for the levelling bulb to the back of the plate for the apparatus and place it into it.
5. Screw the two platinum electrodes onto the bottom of the glass apparatus. To do so, unscrew the two plastic caps.
6. Push the plastic caps and the seals to the metal end of the electrodes and screw the plastic caps back onto the glass apparatus.
7. Connect the hose to the levelling bulb and connect it to the electrolysis apparatus via the free screw connection in the centre.
8. Connect the platinum electrode to the digital multimeter P at the sockets labelled “Output” using the longer connecting leads.
9. Insert the other two connecting leads to the sockets labelled “Input” and connect to the DC power supply.

Preparation of the experiment

1. Since the conductivity of distilled water is too low, the apparatus is filled with dilute sulfuric acid.
2. Before running the test, further dilute the 2 N sulfuric acid. To do so, mix 150 ml of distilled water with 50 ml of the sulfuric acid.

Note: Always start with water, then add acid. Otherwise, too much heat will be generated and the sulfuric acid might squirt.

3. Fill the apparatus with the diluted acid through the levelling bulb. To do so, open the valve at the two shoulders.
4. When filling, make sure that no air bubbles remain at the electrodes and then close the two valves again.

Performing the experiment

1. At the start of the experiment, turn on the DC power supply and set it to 10V. Then, turn on the digital multimeter and record the start time.

Note: There should be rising bubbles observed at both platinum electrodes; these will collect at the two shoulders.

2. After about 15 minutes, the experiment can be ended. To do so, turn off the DC power supply and record the end time and the current at that time.
3. The respective volumes of gas generated can now be read off at the anode and cathode.
4. Read off the gas volumes at ambient pressure. Lower the levelling bulb so that the liquid level in the levelling bulb is at the same height as the liquid level of the respective shoulder.
5. Record the temperature during the experiment using the thermometer.

Observation

As soon as the voltage of 10 V is turned on, gas bubbles will begin to rise at the two platinum electrodes. The measured current *I* can be read off at the digital multimeter P. Furthermore, in the shoulder with the cathode, which is where hydrogen is generated, the gas volume is rising twice as fast. This is because water has twice as many hydrogen atoms as it has oxygen atoms, and oxygen forms at the anode. After a reaction time of at least 15 minutes, the experiment can be stopped and the precise volume, current, temperature and time can be recorded.

Evaluation

The evaluation of the experiment can be done in two ways, depending on the degree of knowledge of the students. On the one hand, Avogadro's Law can be used (SI) or the Faraday constant can be calculated using the general gas equation (SII).

For the calculation, the values listed in Table 1 are required; these values were determined during the experiment. The values for current *I*, time *t*; temperature *T* and volume for hydrogen and oxygen are experimentally determined. The value for the voltage remains fixed since a voltage of 10 V was set at the power supply for the experiment. For air pressure, the standard air pressure of 10^5 Pa or 10^5 Nm^{-2} is used.

Tab. 1 Required values to determine the Faraday constants.

Parameters	Measured values
I	0.31 A
U	10 V
t	900 a
p	10^5 Pa = 10000 hPa = 10^5 Nm^{-2}
T	22 °C = 295 K
***V* (H_2)**	35 ml = 3.5 • 10^{-6} m^3
***V* (O_2)**	17.5 ml = 1.75 • 10^{-6} m^3

Determining the Faraday constant using Avogadro's law

To calculate the constants using Avogadro's law, use the following formula:

$$\frac{p_0 \cdot V_0}{T_0} = \frac{p_1 \cdot V_1}{T_1}$$

Here, standard conditions are assumed for pressure p_0 and temperature T_0 , which means that P_0 = 1013 hPa and T_0 = 273 K. The values for pressure p_1, temperature T_1 and volume V_1 can be found in Table 1.

The formula is solved for volume V_0 for purposes of the calculation.

$$V_0 = \frac{p_1 \cdot V_1 \cdot T_0}{T_1 \cdot p_0}$$

$$V_0 = \frac{1000 \text{ hPa} \cdot 35 \text{ ml} \cdot 273 \text{ K}}{1013 \text{ hPa} \cdot 295 \text{ K}}$$

$$V_0 = 31.97 \text{ ml}$$

Under normal conditions, 1 mole of gas takes up 22.4 l. In order to calculate the moles of hydrogen gas present in V_0, use the value for V_0 in the following formula.

$$n\,(H_2) = \frac{V_0}{22.4 \text{ l}} = 1.4 \text{ mmol}$$

To precipitate this amount, I = 0.31 A flowed in t = 900 s; this corresponds to multiplying the current I and the time t to get 279 As. To obtain the value for 1 mole, divide this by 1.4 *10^{-3} moles.

Then, the Faraday constant F for H_2 equals a value of 199,285 As/mol. However, since in H_2, z = 2 hydrogens (H), the value is divided again by 2.

This gives a value of F = 99,643 As/mol.

Determining the Faraday constant using the general gas equation

To determine the Faraday constant F, the moles n of hydrogen are first calculated using the ideal gas equation.

$$p \cdot V = n \cdot R \cdot T$$

This equation is solved for moles n of hydrogen.

$$n_{H_2} = \frac{p \cdot V}{R \cdot T}$$

The result is then multiplied by 2 since hydrogen is a diatomic gas, in order to obtain the precise number of moles generated.

The Faraday constant is defined as:

$$F = \frac{I \cdot t}{n}$$

The volume of hydrogen generated is converted to a number of moles using the ideal gas equation. To do so, the values from Table 1 are first used in the formula for the ideal gas equation to calculate $n(H_2)$.

$$n_{H_2} = \frac{10^5 \text{ Nm}^{-2} \cdot 3.5 \cdot 10^{-6} \text{ m}^3}{8.32 \frac{\text{Nm}}{\text{K}} \cdot 295 \text{ K}}$$

$$n_{H_2} = 1.4 \text{ mmol}$$

Hydrogen is a diatomic gas, which is why the determined number of moles must be multiplied by 2 in order to find out how many moles of hydrogen (H) were generated. In this case it is 2.8 mmol.

The Faraday constant can now be calculated using the following formula.

$$F = I \cdot t \cdot \frac{1}{n}$$

$$F = \cdot \frac{0.31 \text{ A} \cdot 900 \text{ s}}{2.8 \cdot 10^{-3} \text{ mol}}$$

$$F = 99{,}643 \frac{\text{As}}{\text{mol}}$$

The theoretical value for the Faraday constant is 96,500 As/mol.

Results

In this experiment, the Faraday constant is determined through electrolytic decomposition of water. In the process, water is split into its gaseous components. From the volume of the hydrogen generated, the duration of the experiment, the ambient temperature and the current measured in the process, the Faraday constant can be calculated. In this experiment a Faraday constant of 99,643 As/mol was determined using both calculation methods, which corresponds to a deviation of 3 % from the theoretical value. This is within normal measurement precision. For both calculations, the same results were found since both Avogadro's law and the general gas equation are based on the fact that all gases contain the same number of particles at the same temperature and volumes. The general gas constant R was also introduced here for this purpose. Since in both calculations the same volumes were applied, this provided the same number of moles of hydrogen. Since the amount of charge Q is the same and the Faraday constant is a natural constant, 1 mol of a material always requires 96,500 As/mol to precipitate the same number of moles at the same amount of charge.

Cleaning and disposal

At the end of the experiment, the water decomposition apparatus can remain filled and is therefore ready to use for another experiment.

If the apparatus is emptied, the dilute sulfuric acid can be disposed of in the laboratory sink with plenty of water.