Electricity

Current and the transport of charge

PHYSICS EXPERIMENT

Electrolysis

DETERMINATION OF THE FARADAY CONSTANT

- Production of hydrogen by means of electrolysis and determining the volume of the hydrogen *V*.
- Determining the charge *Q* by measuring the current as a function of time *I*(*t*).
- Calculating the Faraday constant *F*.

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BASIC PRINCIPLES

Electrolysis is the name given to the splitting or dissociation of a chemical bond due to the action of an electric current. The process of electrical conduction is associated with decomposition of the substance in question such that the charge transported *Q* and the quantity in moles *n* of material which has undergone dissociation are proportional to one another. The constant of proportionality is called the Faraday constant *F* and is a fundamental physical constant.

To be more precise regarding the proportionality between the charge *Q* and the number of moles *n* of dissociated material, we actually need to take into account a multiplier *z*, the valency number for the dissociated ions. The following is true:

(1) $Q = F \cdot n \cdot z$

Once that quantity is known, the Faraday constant can therefore be determined by measuring the charge *Q* and the number of moles *n* involved in an electrolytic process.

In this experiment, the electrolysis of water will cause a certain quantity of hydrogen and oxygen to be produced. In order to determine the quantity of charge *Q* transported during this process, the change in electric current over time *I*(*t*) will be measured and then the charge *Q* can be derived by integration:

(2) $Q = \int I(t)\,dt$.

The number of moles of dissociated hydrogen ions n_H is determined from the room temperature ϑ and the pressure *p* exerted from outside on the collected volume of hydrogen V_{H2}. However, it is necessary to take into account that hydrogen is collected in its molecular form, so that each individual hydrogen molecule actually means that two hydrogen ions were dissociated. The following can therefore be derived from the equation of state for an ideal gas.

(3) $n_H = 2 \cdot \frac{p \cdot V_{H2}}{R \cdot T}$

$R = 8{,}314 \frac{J}{mol \cdot K}$ = universal gas constant.

Due to the low conductivity of distilled water, a dilute sulphuric acid solution of concentration 1 mol/l will be used to demonstrate the electrolysis of water.

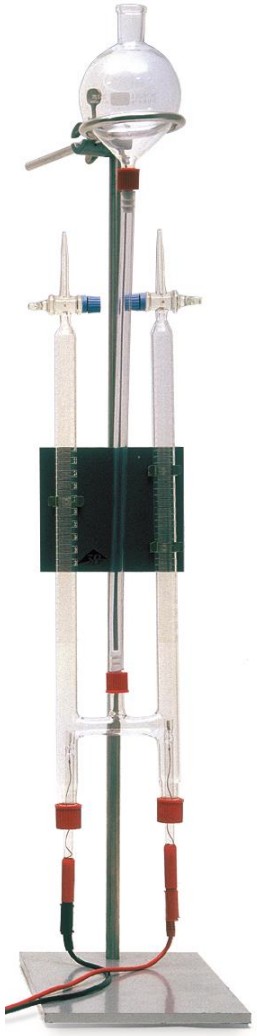

Fig. 1: Hofmann's water decomposition apparatus

LIST OF APPARATUS

1 Hofmann water decompo. apparatus	U14332	1002899
1 DC power supply, 0 − 20 V, 0 − 5 A	U33020	1003311/2
1 Digital multimeter with memory	U118241	1008631
1 Set of 15 experiment leads, 75 cm	U13800	1002840

Additionally required:

1 Stable tube-type thermometer	U16115	1003013
1 Aneroid barometer F	U29948	1010232

Sulphuric acid, 1 mol/l

SAFETY INSTRUCTIONS

Dilute sulphuric acid is an irritant to skin and eyes.

- Wear protective goggles providing full eye coverage, neoprene or vinyl gloves and a lab coat.
- If the acid should come into contact with eyes or skin, immediately wash and rinse thoroughly with water and consult a doctor.

SET-UP

Setting up Hofmann's water decomposition apparatus

- Assemble Hofmann's water decomposition apparatus as per instructions and place it inside a suitable receptacle for collecting liquid if required.
- First attach the levelling bulb as far up as possible on the stand rod (Fig. 1). Pull the support ring forward out of the clamp as far as it will go.
- Open both the ground glass valves on the gas collection tubes.
- Pour about 200 ml of dilute sulphuric acid from the storage bottle into a suitable glass beaker.
- Carefully fill the levelling bulb with sulphuric acid from the beaker. Put the spout of the beaker inside the rim of the levelling bulb. As you fill it, reduce the height of the levelling bulb step by step until the gas collection tubes are completely full. Once the filling procedure is complete, the height of the filling bulb should be such that the liquid level in the levelling bulb itself and that in the two gas collection tubes are initially the same and at the same level as the ground glass valves (see Fig. 2 top).
- Connect the negative pole of the DC power supply to the electrode for the left-hand gas collection tube and introduce a digital multimeter in between in order to measure the current (see Fig. 2 top). Connect the positive pole of the DC power supply to the electrode for the right-hand collection tube.

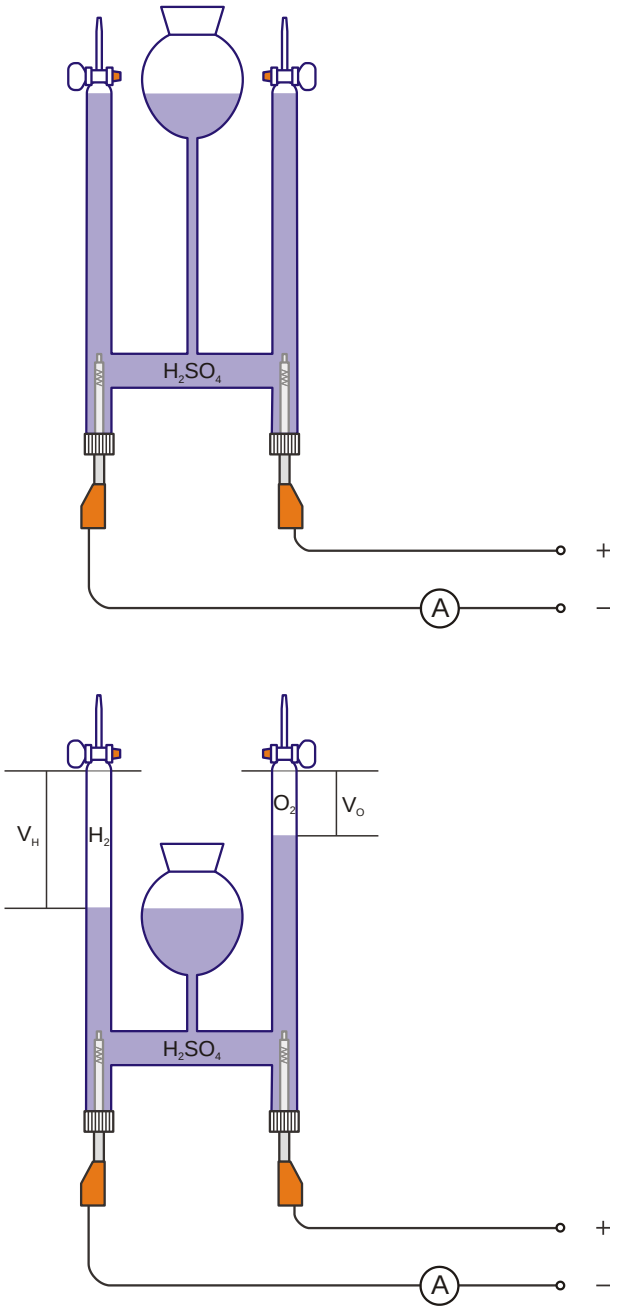

Fig. 2: Schematic of the measurement set-up at the start of measurements (top) and at completion of them (bottom).

Installation of digital multimeter software

We will not be using the software supplied with the digital multimeter, but a more recent version.

- *Do not yet* connect the digital multimeter to a computer.
- Download the software (rar file) from: www.3bscientific.de/datenbank/download/Software-for-1008631.zip

- Expand the rar file into a separate folder of its own.
- Run setup.exe and carry out instructions.

Settting up the digital multimeter

- Connect the computer to the computer with the help of the optical USB cable provided.
- Turn on the digital multimeter whilst simultaneously holding down the “PC LINK” key. “PC-LINK” will be shown on the digital multimeter’s display at the top right. The digital multimeter should then be detected automatically by the computer the first time it is used and its software installed.
- Run the software. Click “Pause” on the menu bar. The message “Logging halted – Click Pause again to continue” will be shown in the bottom left corner.
- Click “Connection” on the menu bar, select hand-held multimeter 3415 from under “Device” and confirm by clicking “OK”.
- Click “Connection” again and select the relevant COM port under “Connect”. Since the system will be paused (see above), the digital multimeter will not yet start recording measurements.
- Click “Advanced” on the menu bar and select “Interval...”. In the pop-up window which opens (“Set Interval”), enter 00:00:01 under “Value”, i.e. 1 measurement will be recorded every second.

EXPERIMENT PROCEDURE

Preparation

- Close both the ground glass valves.
- Turn on the DC power supply, set the maximum voltage V_0 = 20 V (I ≈ 0.75 A) and start the electrolysis without yet recording any measurements. Let it run for about 5 minutes so that the liquid can become saturated with gas.
- Turn on the power at voltage V_0.
- Carefully open both the ground glass valves so that the H_2 can be collected in the left-hand collection tube and O_2 in the right-hand one. Allow the liquid to settle to its original level.

Measurement

- Close both the ground glass valves again.
- Turn on the power with voltage $V_0 = 20$ V.
- Observe how gas develops in the H_2 gas collection tube (negative pole) of the water dissociation apparatus and lower the levelling bulb in such a way that the liquid level in the levelling bulb and in the H_2 gas collection tube remain the same (Fig. 2 bottom).

As soon as the liquid level has reached the 5-ml mark,

- Click “Pause” on the software’s menu bar in order to start taking measurements. The current will gradual increase by about 5 mA per minute.

As soon as the liquid level has reached the 25-ml mark,

- Click “Pause” on the software’s menu bar once again in order to stop the measurements and turn off the power supply.
- Click “File” on the software’s menu bar and save the measurement data using the “Save...” option to “csv” format (for Excel®).
- Measure the room temperature θ and air pressure p and make a note of both values.

SAMPLE MEASUREMENTS

Initial volume V_1: 5 cm^3

Final volume V_2: 25 cm^3

Room temperature θ: 27.5°C

Air pressure p: 1012 hPa

Index	DateTime	Value	Unit	UValue	UUnit
0	06.07.2015 17:56:11	0,757	A	0,757	A
1	06.07.2015 17:56:13	0,757	A	0,757	A
2	06.07.2015 17:56:14	0,757	A	0,757	A
3	06.07.2015 17:56:15	0,757	A	0,757	A
4	06.07.2015 17:56:16	0,757	A	0,757	A
5	06.07.2015 17:56:17	0,757	A	0,757	A
6	06.07.2015 17:56:18	0,757	A	0,757	A
7	06.07.2015 17:56:19	0,757	A	0,757	A
8	06.07.2015 17:56:20	0,757	A	0,757	A
9	06.07.2015 17:56:21	0,757	A	0,757	A
10	06.07.2015 17:56:22	0,757	A	0,757	A
11	06.07.2015 17:56:23	0,757	A	0,757	A
12	06.07.2015 17:56:24	0,757	A	0,757	A
13	06.07.2015 17:56:25	0,757	A	0,757	A
14	06.07.2015 17:56:27	0,757	A	0,757	A
15	06.07.2015 17:56:28	0,757	A	0,757	A
16	06.07.2015 17:56:29	0,757	A	0,757	A
17	06.07.2015 17:56:30	0,757	A	0,757	A
18	06.07.2015 17:56:31	0,757	A	0,757	A
19	06.07.2015 17:56:32	0,757	A	0,757	A
20	06.07.2015 17:56:33	0,757	A	0,757	A
21	06.07.2015 17:56:34	0,757	A	0,757	A
22	06.07.2015 17:56:35	0,757	A	0,757	A
23	06.07.2015 17:56:36	0,757	A	0,757	A
24	06.07.2015 17:56:37	0,757	A	0,757	A
25	06.07.2015 17:56:38	0,757	A	0,757	A
26	06.07.2015 17:56:40	0,757	A	0,757	A
27	06.07.2015 17:56:41	0,757	A	0,757	A
28	06.07.2015 17:56:42	0,757	A	0,757	A
29	06.07.2015 17:56:43	0,757	A	0,757	A
30	06.07.2015 17:56:44	0,757	A	0,757	A
31	06.07.2015 17:56:45	0,759	A	0,759	A
32	06.07.2015 17:56:46	0,759	A	0,759	A
33	06.07.2015 17:56:47	0,759	A	0,759	A
34	06.07.2015 17:56:48	0,759	A	0,759	A
35	06.07.2015 17:56:49	0,759	A	0,759	A
36	06.07.2015 17:56:50	0,759	A	0,759	A
37	06.07.2015 17:56:51	0,759	A	0,759	A
38	06.07.2015 17:56:53	0,759	A	0,759	A
39	06.07.2015 17:56:54	0,757	A	0,757	A
40	06.07.2015 17:56:55	0,757	A	0,757	A
41	06.07.2015 17:56:56	0,757	A	0,757	A
42	06.07.2015 17:56:57	0,759	A	0,759	A
43	06.07.2015 17:56:58	0,757	A	0,757	A
44	06.07.2015 17:56:59	0,759	A	0,759	A
...	...	...	...	...	...
198	06.07.2015 17:59:45	0,769	A	0,769	A

Fig. 3: Screenshot of measurements made by digital multimeter in Excel® (extract from csv file).

EVALUATION

- Open the csv file with measurements of current as a function of time in Excel®, for example (Fig. 3).
- Convert the time values in the “DateTime” into “Number” format, specifying 5 decimal places.
- Subtract the number in the first cell of the “DateTime” column from all of the entries in that column.
- Multiply all the numbers in the “DateTime” column by 86400 and then convert the format to “Number” with 0 decimal places. The time values will then be in seconds (Fig. 4).

Index	DateTime	Value	Unit	UValue	UUnit
0	0	0,757	A	0,757	A
1	2	0,757	A	0,757	A
2	3	0,757	A	0,757	A
3	4	0,757	A	0,757	A
4	5	0,757	A	0,757	A
5	6	0,757	A	0,757	A
6	7	0,757	A	0,757	A
7	8	0,757	A	0,757	A
8	9	0,757	A	0,757	A
9	10	0,757	A	0,757	A
10	11	0,757	A	0,757	A
11	12	0,757	A	0,757	A
12	13	0,757	A	0,757	A
13	14	0,757	A	0,757	A
14	16	0,757	A	0,757	A
15	17	0,757	A	0,757	A
16	18	0,757	A	0,757	A
17	19	0,757	A	0,757	A
18	20	0,757	A	0,757	A
19	21	0,757	A	0,757	A
20	22	0,757	A	0,757	A
21	23	0,757	A	0,757	A
22	24	0,757	A	0,757	A
23	25	0,757	A	0,757	A
24	26	0,757	A	0,757	A
25	27	0,757	A	0,757	A
26	29	0,757	A	0,757	A
27	30	0,757	A	0,757	A
28	31	0,757	A	0,757	A
29	32	0,757	A	0,757	A
30	33	0,757	A	0,757	A
31	34	0,759	A	0,759	A
32	35	0,759	A	0,759	A
33	36	0,759	A	0,759	A
34	37	0,759	A	0,759	A
35	38	0,759	A	0,759	A
36	39	0,759	A	0,759	A
37	40	0,759	A	0,759	A
38	42	0,759	A	0,759	A
39	43	0,757	A	0,757	A
40	44	0,757	A	0,757	A
41	45	0,757	A	0,757	A
42	46	0,759	A	0,759	A
43	47	0,757	A	0,757	A
44	48	0,759	A	0,759	A
...	...	...	...	...	...
198	214	0,769	A	0,769	A

Fig. 4: Screenshot of measurements made by digital multimeter in Excel® (extract from csv file) after modification of date-time format.

- Plot the measurements of current (“Value” column) against the time in seconds (“DateTime” column) in a graph (Fig. 5).

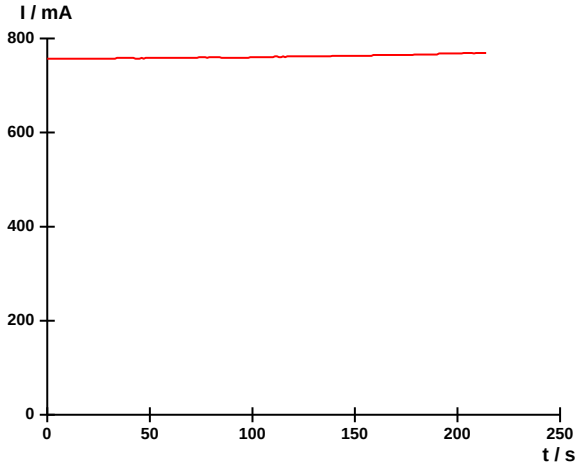

Fig. 5: Current as a function of time

The current rises approximately linearly with time.

- Fit a straight line $I(t) = m \cdot t + k$ to the measurement points:

(4) $m = 6.0 \cdot 10^{-5} \frac{A}{s}$.
$k = 0.7554\,A$

- Determine the charge Q using (2) as follows (t_{max} = 214 s, see Fig. 4):

$$Q = \int_0^{t_{max}} I(t)\,dt = \int_0^{t_{max}} (m \cdot t + k)\,dt$$

(5) $$= \int_0^{t_{max}} m \cdot t\,dt + \int_0^{t_{max}} k\,dt = \frac{1}{2} \cdot m \cdot {t_{max}}^2 + k \cdot t_{max} .$$
$$= 163\,As$$

- Calculate the volume of hydrogen:

(6) $V_{H2} = V_2 - V_1 = 20\,cm^3$.

- Calculate the absolute temperature:

(7) $T = \theta + 273K = 300.5K$.

The multiplier for the number of hydrogen ions z_H = 1. From equations (1) and (3) it is possible to obtain an equation for determining the Faraday constant.

(8) $$F = Q \cdot \frac{R \cdot T}{2 \cdot p \cdot V_{H2} \cdot n_H} = Q \cdot \frac{R \cdot T}{2 \cdot p \cdot V_{H2}} .$$

Using the values calculated in steps (5), (6) and (7) along with the measurement of the atmospheric pressure p, the value obtained is

(9) $$F = 163\,As \cdot \frac{8{,}324 \frac{J}{mol \cdot K} \cdot 300{,}5K}{2 \cdot 1012hPa \cdot 20\,cm^3} = 10{,}1 \cdot 10^4 \frac{As}{mol} .$$

The value determined by measurement is in agreement with the literature-quoted value $F = 9.6 \cdot 10^4$ As/mol to a tolerance of about 5%.

As a comparison, you can also determine the volume of the collected oxygen V_{O2}. It is only half as much as the volume of hydrogen since when water dissociates, it does so into two hydrogen ions and one oxygen ion. However, the multiplier for the oxygen ions z_O = 2.

ADDITIONAL INFORMATION

Systematic errors occur due to oxygen in particular dissolving in the electrolyte, also because gas bubbles get trapped by the walls of the glass and because the temperature of the electrolyte and of the gases both increase as a result of the flow of current itself.

Some of the oxygen atoms released during electrolysis react to form persulphuric acid. For these reasons, the quantity of oxygen collected is slightly less than the amount which has actually dissociated. This is why the quantity of hydrogen is used in order to obtain the results.

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